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AC Hall Mobility and Electrical Conductivity in Amorphous Threshold Switching Semiconductor

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By
G. P. Carver
R. S. Allgaier

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NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

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ac Hall Mobility and Electrical Conductivity in Amorphous Threshold Switching Semiconductors

As part of a program to evaluate the radiation hardness of amorphous semiconductor devices, this report presents the results of transport property studies on bulk samples of the amorphous threshold switching materials. This work was supported by the Advanced Research Projects Agency, work order #1573.

ROBERT WILLIAMSON II
Captain, USN
Commander

W. W. SCANLON
By direction

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FIGURES

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I. INTRODUCTION

The Hall effect plays an important role in the investigation of electronic properties of crystalline solids because it allows carrier density and carrier mobility to be determined separately. In the case of amorphous semiconductors, however, the Hall effect has not yet played such a role because it is difficult to measure, and the results have generally been regarded as unreliable and anomalous.[1]

The Hall measurements are considered anomalous because they do not seem to be consistent with models deduced from other types of measurements obtained earlier on many amorphous materials. A more objective statement would be to say that theoretical models have not been able to account for the unusual combination of properties often found in amorphous semiconductors, viz., a negative Hall coefficient, a positive thermoelectric power, a small ($\sim$0.03 - 0.3 cm^2/V-sec) Hall mobility, and a large pre-exponential factor in the electrical conductivity. The experimental problem has been to separate the relatively small Hall signal from a large, temperature-sensitive, and noisy resistivity voltage.[2,3]

This report (a) describes the design of an apparatus which overcomes some of the problems in measuring the Hall effect in amorphous semiconductors and (b) presents the first results obtained using this apparatus, viz. the Hall mobility, μ_H, and the electrical conductivity, σ, in two threshold switching amorphous semiconductors, $As_{34.5}Te_{27.9}Ge_{15.6}S_{22.0}$ and $As_{35}Te_{40}Ge_7Si_{18}$. The results of the Hall mobility measurements, performed at frequencies between 10 and 100 kHz, include unexpectedly high and extremely frequency-dependent values.

II. THE CORBINO DISC APPARATUS

A new and unique apparatus, based on the Corbino disk geometry, was developed to measure Hall mobilities in the regime of high resistance amorphous semiconductors.[4] The novel feature of the Corbino method is that it avoids the problems of contact effects and large zero field offset voltages (which almost always plague conventional Hall experiments on high resistivity materials) because the signal is detected inductively.

THEORY OF THE MEASUREMENT. The geometry of the Corbino disc experiment is shown in Fig. 1. A radial current flows between the center electrode and the outer rim of the sample. When a magnetic field perpendicular to the plane of the sample is applied, a circular component of current appears. The circular current, I_θ, is the Hall current and is given by[4]

$$I_\theta = \frac{\sigma R_H B I_r}{2\pi} \ln \frac{r_2}{r_1} , \tag{1}$$

where σ is the conductivity, R_H is the Hall coefficient, B is the magnetic flux density, I_r is the total radial current, and r_1 and r_2 are the inner and outer radii of the sample contacts, respectively. By definition, the Hall mobility

$$\mu_H = R_H \sigma ; \tag{2}$$

hence I_θ is directly proportional to μ_H.

The Corbino disc geometry is analogous to an infinitely wide rectangular Hall sample. In both cases, there are no transverse boundaries and therefore no Hall voltage can build up. Instead, the current rotates through the angle θ with respect to the applied radial voltage. In practice, the radial current (and thus the Hall current) is alternating. This is necessary so that the circulating Hall current may be detected inductively by a pickup coil placed near the sample.

Assuming the presence of a single-turn pickup coil of radius a at a distance b from a sample of thickness W and the conditions

$$\begin{aligned} &W \ll r_2, \\ &r_1 \ll r_2, \quad \text{and} \\ &b \ll a , \end{aligned} \tag{3}$$

the induced voltage, V(a), is given by an expression of the form[5,6]

$$V(a) = i\, \omega\, W \int_{r_1}^{r_2} M(r,a)\; J_\theta(r)\, dr ; \tag{4}$$

ω is the frequency of the sample current and M(r,a) is the mutual inductance between the current density element $J_\theta(r)$ and the (single turn) pickup coil.

Evaluation of (4) is only possible under certain approximations suitable for particular frequency ranges.[6] Under "low frequency" conditions (which obtain for amorphous semiconductor samples) the signal voltage induced in a single turn is given by

$$V(a) = i\,\omega\,\sigma\,R_H I_r B \int_{r_1}^{r_2} \frac{M(r,a)\,dr}{2\pi r} . \qquad (5)$$

While it is possible to numerically evaluate (5) for an accurately known geometry, it is more expedient to obtain relative values of V(a) by calibrating the system using a sample whose mobility is known. We have used silver foil for this purpose.

THE SAMPLE HOLDER AND PICKUP COIL. A cutaway view of the sample holder is shown in Fig. 2. The apparatus is constructed of oxygen-free copper and is designed for a solenoidal magnetic field. The current electrode uniformly distributes the current to the sample. To avoid contributions to the pickup voltage from the Hall currents in the electrode itself, radial slots are cut in that part of the electrode where current flow is primarily perpendicular to the magnetic field. The pickup coil is stationary and a screw-on ring rigidly holds the electrode assembly and sample against the coil.

The positioning of the coil on the side of the sample opposite to the center current contact serves to reduce capacitive coupling to the coil. Such coupling is further diminished by wrapping the coil in 25 μm-thick aluminum foil which is grounded and acts as an electrostatic shield. (The sample side of the shield is insulated to avoid shorting to the sample.) At operating frequencies in the audio range, electrostatic shielding of the coil is essential; without such shielding, coupling voltages are large enough to overload the input to the preamplifier.

THE ELECTRONICS. The experimental configuration is best visualized as a transformer, where the primary is the circular Hall current in the disc-shaped sample and the secondary is the pickup coil. The object is to optimize the electrical characteristics of that transformer. With the additional consideration of convenient sample mounting, this viewpoint guided our development of the geometrical configuration just described. In this section we consider the external circuitry, with particular emphasis on proper impedance matching and reduction of the effects of parasitic voltages. A block diagram of the electronics is shown in Fig. 3.

The Primary Circuit. The sample current is supplied by the reference output from a phase sensitive detector (PAR 124). The voltage applied to the sample is measured by an ac voltmeter (Singer 323). A broadband amplifier (GR 1233-A) is sometimes used to increase the available sample voltage. The required characteristics of the current supply circuitry are good phase stability, low distortion and adequate shielding to prevent extraneous pickup by the detection circuit.

The Secondary Circuit. The pickup coil leads are connected directly to the lock-in preamplifier (PAR 118), which is operated in a differential mode. With the low sample current levels necessary to avoid joule heating, the detection circuit must be able to detect extremely small signals. This requires more than just sufficient amplification of a small signal in the lock-in signal channel; the reduction of noise levels and spurious zero-field pickup voltages is essential. These are not independent problems because sources of spurious pickup are themselves the major sources of noise.

Much of the unwanted pickup can be eliminated at the sample. Geometrical factors such as good axial alignment of the current electrode, sample and coil, and uniform radial current distribution in the sample are important.

At kilohertz frequencies an additional source of pickup is capacitative coupling to the coil. Such coupling is especially serious with high resistance samples because voltage levels are relatively higher. (In a sense this effect is the analogy of the Hall probe misalignment voltage which inevitably appears in a conventional geometry Hall experiment on high resistance samples.) Capacitive coupling can be minimized by enclosing the coil in an electrostatic shield, as described earlier, and by operating the lock-in amplifier in a differential input mode. When the coil is balanced with respect to the proximity of its windings to the center current electrode and with respect to the impedance paths through the two output leads, the remaining parasitic coupling voltage appears in common mode and is rejected in large part by the amplifier.

A phase shifting network, the purpose of which was to feed back a nulling signal to cancel zero-field pickup at the input to the lock-in, was built and tested. This approach had been useful in a previous application of the Corbino method.[5] However, the apparent increase in usable sensitivity was itself cancelled by an increase in both noise and drift. Again, we emphasize that the reduction of unwanted pickup at the source is the most desirable approach.

In addition to electrostatic shielding and symmetrical detection, proper impedance matching between coil and preamplifier is necessary. Actually, it is the induced signal which must be matched by the input impedance of the preamplifier. Because the impedance level at which the signal appears partially reflects the primary circuit impedance, it is not equal to the dc resistance of the coil nor to the ac impedance of the coil at the operating frequency. Determination of the signal impedance was accomplished experimentally by resistive loading of an offset voltage induced in the coil by the current in the sample. The offset voltage was produced by temporarily moving the coil, or the center contact to the sample, slightly off-axis. The signal impedance in our apparatus is greater than the dc resistance but less than the ac impedance of the coil.

Phase. The relative phase between the reference voltage and the signal at the lock-in must be determined empirically. If the Corbino "transformer" were ideal, the phase angle between the sample current and the signal in the coil would be 180°. However, neither this phase shift nor the additional phase shifts introduced by distributed capacitance in the cables has been determined. Also, the total phase shift is not a constant of the apparatus partly because of the strong phase dependence of the tuning of the lock-in signal channel and also because of the strong frequency dependence of the mobility (at least in the materials reported here). At each frequency therefore, the lock-in phase control is set to maximize the signal, based on data from mutually orthogonal phase settings.

Noise. When all undesirable pickup has been reduced to a minimum and impedance matching has been optimized, the remaining noise was found to be predominantly 1/f in nature. The sources of such noise[7] are thermal variations and joulian noise in the sample, and fluctuations in the magnetic field. Consequently, analogue smoothing is of limited value.[7] However, signal-to-noise improvement through digital averaging was found to be effective against the 1/f noise. By storing the output of the lock-in amplifier as a function of field in the memory of a signal averager, the accumulated sum of many relatively fast runs are obtained. Low frequency noise excursions thus appear only as baseline variations. In effect, the low frequency cutoff of the experiment is raised due to the shorter measurement time.

DATA ACQUISITION TECHNIQUE. The digital signal averager (Nicolet 1070) programs the magnetic field sweep and accumulates data as a function of field by digitizing the rectified output from the phase sensitive detector. The Hall signal is the difference between the data for opposite magnetic field directions.

The field reversal technique helps to eliminate baseline effects, but it isn't possible to achieve the four reversals usually performed in conventional dc Hall experiments since the current is already alternating. However, because there are no voltage contacts to the sample and because the Corbino disc experiment is an ac method, it is insensitive to thermoelectric and thermomagnetic effects,[5] and thus there is no need for the complete series of reversals.

The magnet is a liquid nitrogen-cooled, solenoidal copper magnet capable of reaching 0.3 Tesla. The magnetic field sweep period is about five seconds from zero to full field and back. (Actually the field sweep begins at about 0.08 Tesla rather than zero. This helps reduce bursts of noise which occur at the turnaround of the field. In addition, a 5 mHy coil is connected across the preamplifier to further reduce the effect.)

A typical measurement involves perhaps 64 sweeps in each field direction, depending upon the signal-to-noise ratio. The results from the two field directions are subtracted electronically and the difference plotted by an x-y recorder.

The signal levels encountered in the Hall mobility measurements described in this report are between a few and a few hundred nanovolts. Sample current levels were less than a microampere, in order to avoid Joule heating of the samples. It should be noted however that this apparatus has also been successfully operated on metallic foil samples with current levels up to ten amperes and to frequencies as low as eleven Hz.

A constant temperature environment is provided by a heater wound on a copper tube which fits inside the glass dewar. The dewar itself fits inside the solenoidal magnet, and is therefore in the liquid nitrogen bath used to cool the magnet. A copper-constantan thermocouple mounted on the heater provides the input to a microvolt-ammeter (Keithley 150 AR) whose 0-10 volt output supplies an error voltage to a dc power supply. The dc supply powers the heater winding. The equilibrium temperature is set by adjusting the zero-suppress control on the Keithley.

Accurate reading of the temperature is obtained from a 200 Ω platinum resistor mounted inside the copper Corbino holder. (The resistor is not labeled in Fig. 2, but is located near the top of the holder.) A constant-current power supply and a potentiometer (L and N K-2) monitor its resistance.

An earlier arrangement whereby the heater windings were wrapped on the Corbino sample holder[4] was found to be inadequate. The center of the sample (which is not heat sinked except by the rest of the sample itself) was cooled via the copper wire leading around the outside of the holder and heater. The result was a gradual change in the signal magnitude and phase as the inside of the dewar, and the center of the sample, cooled during a run.

<u>CALIBRATION</u>. While it is possible to calculate expected signal voltages on the basis of equation (5), it is more practical to experimentally calibrate the apparatus using a sample of known mobility. We used a silver foil sample for this purpose. We also measured a variety of metallic samples to investigate the accuracy, reproducibility, and such effects as the sample current and frequency dependence of the signal voltage.[4] The induced signal was found to be linear in each of these parameters.

One other calibration consideration was investigated, that of the effect of sample thickness. As the thickness of the sample increases so does the average distance from the coil to the circulating Hall currents. The dependence of the signal on sample-to-coil distance was measured, again using a metal foil sample. The sensitivity calibration for the thicker glass samples is then corrected by a factor given by the integral of an empirical curve.[4]

III. THE SAMPLES

The materials were the threshold switching compositions, $As_{34.5}Te_{27.9}Ge_{15.6}S_{22}$ (designated "Type A") and $As_{35}Te_{40}Ge_{7}Si_{18}$ ("Type B"). Samples were fabricated from the melt by Energy Conversion Devices, Inc. to fit the current electrode configuration of the Corbino disc apparatus. Thus, the samples were wafers, approximately 1.5 cm in diameter and 0.12 cm in thickness. A 1 mm diameter spot of molybdenum was deposited on one face of each sample to accept the center contact.

Virtually noise free electrical contact between the copper current electrode and the samples was made using a room temperature liquid indium-mercury alloy.[8] The liquid metal is easily applied to the sample around the rim and on the Mo center spot.

There is evidence that the alloy is not inert with respect to the amorphous samples. A polished surface of each of the amorphous compositions that were studied appears streaked with a dull, grayish-white pattern after the liquid alloy is removed. Possibly one of the metal components is able to diffuse into the glass. Whatever the explanation, the effect is only on the surface, as merely a few seconds repolishing with 0.1 μm abrasive restores the original shiny appearance of the surface. Also, after the surface dullness was removed, there was no permanent effect on the conductivity of the sample.

The measured values of the Hall mobility are insensitive to any effects at the contacts because those parts of the sample near the rim and in the center are not flux linked to the pickup coil.[4] Whatever the nature of the reaction between the In-Hg alloy and the amorphous samples, the effect is to improve the electrical contacts for the Corbino disc experiment and reduce the pickup noise to low levels. (In the case of another multicomponent glass we have studied, $Tl_2SeAs_2Te_3$, noise levels were consistently higher. We feel this was a property of that material, rather than the contacts.)

No special precautions were taken in handling and storing the samples other than those necessary to maintain cleanliness (e.g. fingerprint free surfaces). Except in the case of the van der Pauw measurements, none of the properties of the samples showed any sign of degradation under routine experimentation. (The four-point van der Pauw measurements will be discussed in a subsequent section.)

There were, however, a few incidents which demonstrated that a contaminated sample surface increases the sample conductance. For example, on one occasion during an especially humid day, frost from the inside of the dewar system accidentally fell onto a sample as it was being replaced. A large increase in the sample conductance resulted. Repeated cleansing with acetone followed by pure distilled water was required to restore the original conductance.

IV. THE MEASUREMENTS

The transport properties which were studied were the electrical conductivity and the Hall mobility. The conductivity, σ, was measured from dc to frequencies as high as 100 kHz over a temperature range from 220 K to 352 K. The Hall mobility, μ_H, was measured at two different temperatures for each material (approx. 220 K and 250 K) and at frequencies from 10 kHz to 100 kHz. One sample of Type A and two samples of Type B were studied. In addition the mobility at 100 kHz for one sample of Type B material, was measured between 237 and 308 K. All measurements were performed using the Corbino disc apparatus, with two exceptions:

1. The frequency dependence of the mobility was verified for sample B-2 using a modified van der Pauw technique, and

2. The absolute conductivity of sample B-2 was measured separately between the flat faces of the wafer.

THE CONDUCTIVITY. The ac conductivity of the samples was measured only after it became obvious that it was needed to provide a calibration for the Hall mobility measurements. Subsequently however, more careful measurements were made between 10 and 100 kHz to determine whether any unusual frequency dependence, similar to that of the Hall mobility, could be observed in the conductivity. The ac conductance of the samples was determined using a resistance-capacitance bridge (GR 1615A). The signal generator was an oscillator (HP 3300A) and the lock-in amplifier served as the detector.

It was not possible to work in a true three terminal configuration because of the way the Corbino probe is grounded. However, great care was taken to avoid spurious contributions to the measurements. In addition, the lock-in, operated in the phase sensitive mode, was adjusted to be orthogonal to the capacitive unbalance at each frequency. The bridge was brought to a coarse null visually, using an oscilloscope to monitor the signal channel output of the lock-in, and then carefully balanced using the phase-sensitive output. A change of one unit in the highest resolution decade on the bridge was easily observable.

dc conductance measurements were made simply with a megohmmeter (GR 1862-B).

All conductance measurements were made while the samples were mounted in the Corbino sample holder and were converted to conductivity by a single calibration at 298 K. In the case of sample B-2, the dc conductance between the flat faces of the sample was measured separately. The value of the conductivity for type A material was that quoted by ECD when the samples were supplied.

It is possible to calculate the conductivity from the Corbino sample configuration, but the uncertainties would be large. For an

ideal disc-like sample, the conductivity, σ, is given by:

$$\sigma = \frac{G \ln \frac{r_2}{r_1}}{2\pi W} \tag{6}$$

where G is the measured conductance. The ratio $\frac{r_2}{r_1}$ is the troublesome quantity, especially in our situation where the center contact does not go through the sample but is only on one face.

THE HALL MOBILITY. At first it was thought that a single measurement on the Corbino disc apparatus would lead directly to the Hall mobility. However, in the case of these high resistance samples it was not possible to measure the current directly because of the larger capacitive losses in the cables. Also because of the high resistance of the samples, it was not desirable to add any other connections (e.g. inserting a resistor in the current line inside the current electrode) to measure only that part of the current flowing into the sample. However, there was no voltage drop between the voltage source and the sample. Hence the sample voltage and conductance were used to calculate the current for the mobility measurements. The current was usually less than one microampere.

The experimental setup was described earlier. Examples of the raw data, as traced out by the x-y recorder, are shown in Fig. 4. The signal is taken to be the difference in the vertical height across the graph paper of a line drawn through the trace. In order to calculate the mobility, the signal is divided by the frequency, multiplied by a calibration factor determined from the signal generated by a silver foil sample (μ = 57.1 cm^2/V-sec), normalized to the number of sweeps, the amplification, and the sample current at the given frequency, and finally adjusted to account for the thickness of the sample. It should be noted that for constant mobility, the signal is approximately proportional to ω^2 because of the ω dependence of the pickup [Eq. (5)] and the $\sim\omega$ dependence of the conductivity. Thus, a given mobility will result in a signal about 100 times larger at 100 kHz than at 10 kHz (assuming the sample voltage is constant).

The magnetoresistance, which was observed to be negative for these materials, appears in second order in the signal and was neglected.

THE VAN DER PAUW MEASUREMENT. Sample B-2 was measured in a van der Pauw (four-point) configuration. This experiment was done to obtain independent evidence for the frequency dependence of the Hall mobility, even though many tests were performed to eliminate the small possibility that the observed frequency dependence was spurious or was an artifact of the Corbino sample holder. (These efforts will be described in the next section.)

A special holder was constructed for the four-point Hall measurement. Contact to the sample was made at four symmetrical points near the edge of one face with indium-mercury wetted platinum wire. A high impedance differential preamplifier (PAR 116) was used in the lock-in. Although no quantitative evaluation of the Hall coefficient was possible, because the 10^8 ohm preamplifier input impedance is not sufficiently high to avoid loading the sample current distribution, the dependence of the Hall signal on frequency, and sign, was preserved. (In one sense this might be considered a three electrode geometry[9].)

The signals were well behaved in that they appeared at the correct phase and were linear in the magnetic field. Thus a second benefit was reaped from this experiment: The identification of the sign of the Hall effect. It was not explicitly discussed earlier, but the uncertain phase relationship between the sample voltage and the induced signal in the Corbino method (specifically the variation of the induced signal phase due to the strong frequency dependence of the signal) prevented reliable determination of the sign of the carriers which dominate the Hall mobility signal. In contrast, the Hall voltage appearing across the Hall probes in the four-point method is directly coupled to the electric field in the sample. Simple geometrical constraints followed by a consistent measurement of a germanium sample of known type confirmed the identification of the sign (positive) of the Hall effect in the amorphous samples.

A deterioration in the signal obtained in the van der Pauw configuration was observed over a period of several days. (The data shown later is the first run. The results of subsequent runs were not equal in accuracy and reliability.) The deterioration was ascribed to contamination of the surface which occurred, we believe, because the sample was not enclosed, as in the Corbino disc measurements, nor was the insert dewar sealed. Visual examination of the sample at the completion of the experiment revealed that the surface of the sample had indeed become dirty.

V. THE RESULTS

THE CONDUCTIVITY. The conductivity as a function of temperature is plotted in Figs. 5 and 6 for Type A and Type B material respectively. From the dc values an activation energy of 0.60 eV is obtained for both materials. The ac data show the usual weakly temperature-dependence regime at sufficiently high frequency and/or low temperature.

The conductivity as a function of frequency at several different temperatures is shown in Figs. 7 and 8. The results are qualitatively the same as those for other multicomponent amorphous chalcogenides.[10,11]

As mentioned earlier, a more careful study of the conductance of the samples was carried out over the frequency range 10 to 100 kHz. The results are shown in Figs. 9 and 10. There appears to be a change

in slope of the conductivity-frequency data, and lines have been superimposed to indicate the two regions of different slope. That there actually is an abrupt change in slope (as opposed to a gentle unward curve) is demonstrated in Figs. 11 and 12. Here the data have been least-squares fit at the lower frequencies and the difference between the data and the mathematical fit is plotted against frequency over the entire frequency range. (The ordinate scale, 1000 x log σ/σ', is just the magnified value of the distance, on the graphs of Figs. 9 and 10, between each data point and an (extended) line fit to the lower frequency points.) The graphs show that there are indeed two linear regions on the log conductance vs frequency graphs. The value for the slope of the lines in each of these regions was obtained from the computer fit.

The abrupt changes in slope, at about 60 kHz for Type A material and 50 kHz for Type B material, occur near the minimum in the most pronounced valley in the μ_H vs frequency data at 220 K.

<u>THE HALL MOBILITY</u>. The results of the Hall mobility measurements using the Corbino disc apparatus are shown in Figs. 13 through 17. The measurements were made at temperatures of 220 K and 255 K on a sample of Type A material ($As_{34.5}Te_{27.9}Ge_{15.6}S_{22}$, sample A-1), at 241 K on a sample of Type B material ($As_{35}Te_{40}Ge_{7}Si_{18}$, sample B-1), and at 220 K and 250 K on a second sample of Type B material (sample B-2). The frequency range was 10 to 100 kHz.

The temperatures were not special; they were chosen for convenience. The frequency range was limited at the lower end by noise from the magnetic field sweep and at the upper end by the operating range of the lock-in amplifier. (The frequency range will be extended in both directions in the future.) At least one additional peak has been observed below 10 kHz. However, the calibration does not extend below 10 kHz, because the impedance of the 5 mHy coil across the preamplifier leads begins to load the signal.

The high values and strong frequency dependence of the mobility were completely unexpected. Such results have not been observed before in any material. (Of course this may be primarily due to the fact that no mobility measurements at these frequencies could be found in the literature.) Therefore, efforts were made to verify the reality of the data and to eliminate any possibility that they might be due to spurious effects or experimental artifacts. These efforts included the following tests:

1. All cables and connections were changed, additional inductance was added to the pickup coil circuit, a different preamplifier (PAR 116) was tried, and various modes of operation of the lock-in detector were used, including a separate external oscillator, to determine whether any change would occur in the frequency dependence of the mobility. The results were negative.

2. The mobility in a silver sample was measured as a function of frequency under the same conditions as the amorphous samples, except that the impedance of the sample was unavoidably lower. The signals were linear in frequency (i.e. the mobility was not a function of frequency, as expected).

3. No signal at all could be observed when a polystyrene disc, whose impedance is extremely high, was substituted for the amorphous samples. Also, no signal was observed without any sample in place.

4. The signal in the amorphous samples was linear in magnetic field strength and sample voltage, as a true Hall signal should be. (Certain puzzling exceptions are noted later.)

5. The separate four-point van der Pauw measurement described earlier was made on sample B-2. A special sample holder was constructed for this purpose. The experiment was performed using the same magnet and external circuitry, except for the high impedance preamplifier. The results are shown in Fig. 18. As explained earlier the data cannot be calibrated nor unfortunately can they be compared directly with the Corbino data for sample B-2 because an intermediate temperature was inadvertantly chosen. However, the similarity between the two results is unmistakable.

In addition, the lack of a similar frequency dependence in the conductivity data, taken with the samples still in the Corbino probe, and the large changes in the mobility with temperature lend extra weight to the argument that no spurious resonances in the circuitry are responsible for the results and that the data are reliable. (Unfortunately, the lack of structure in the conductivity-frequency data also makes a comprehensive interpretation more elusive.)

Prior to obtaining the mobility vs frequency data, measurements were made on sample B-1 at constant frequency (100 kHz) as a function of temperature. These results are shown in Fig. 19. But it is no longer clear whether the temperature dependence is purely a temperature effect or whether it includes effects of the peaks in the mobility changing frequency with temperature. However, the decreasing mobility with increasing temperature is a general feature of all the μ_H-frequency data and is opposite to the temperature dependence of the conductivity.

There are other features of the mobility results which cannot be seen on the graphs but which are important nevertheless because they bear on the reliability and the interpretation of the results:

1. The data were taken in an almost random order with respect to frequency. The reproducibility of the results was well within 10% during the same day's run. From day to day the reproducibility was usually within 20%, even if the sample had been warmed to room temperature overnight.

2. At most frequencies, the signal was linear in magnetic field. (See Figs. 4a to 4d) However, at frequencies on the steep sides of peaks, where $\Delta\mu/\Delta\omega$ was large, the signal tended to exhibit a kink. The most dramatic example of this effect is shown in Fig. 4e. Other, more typical examples are shown in Figs. 4f and 4g. The slope of the signal is the same above and below the kink. No explanation of this phenomenon has been found.

3. The error limits shown on the points in Figs. 13-17 reflect random uncertainties in the signal and other relevant experimental parameters. Systematic errors may be somewhat larger.

4. It is not known whether there is any finer structure in the μ_H-frequency curves. As quoted above, reproducibility in the signal was not worse than about 20%. However at a few specific frequencies the reproducibility was much worse if the frequency was adjusted and then returned to a given value. The largest such effect occurred at 70 kHz on sample A-1 at 220 K (Fig. 13).

IV. DISCUSSION OF THE RESULTS

The dc Hall mobility in amorphous semiconductors is almost always negative (i.e., corresponding to electrons) and of the order of 1 cm^2/V-sec or less.[3,12] Furthermore it is usually temperature-independent or increases slightly with increasing temperature. Thus the extremely large, positive values, together with their oscillatory dependence on frequency and negative temperature coefficient reported here represent new and unexpected results.

It may seem at first glance that this Hall mobility behavior cannot be consistent with the conductivity measurements obtained on the same material. But because of the different averaging procedures appropriate for μ_H and σ, it is possible to account for both results, as the following analysis demonstrates.

Suppose there are two kinds of carriers present; then

$$\sigma = n_1 e_1 \mu_1 + n_2 e_2 \mu_2 \tag{7}$$

where n_i, e_i and μ_i are the density, charge, and mobility of the i-th carrier type. Note that each term is positive, since e_i and μ_i always have the same sign. On the other hand,

$$\mu_H = \frac{(n_1 e_1 \mu_1)\mu_1 + (n_2 e_2 \mu_2)\mu_2}{n_1 e_1 \mu_1 + n_2 e_2 \mu_2} ; \tag{8}$$

in this case, the sign of each term in the numerator is determined by the sign of μ_i.

Suppose the second term in Eq. (7) represents the high mobility carriers. If they are to have only a small effect on the behavior of σ, we may assume that $n_2 e_2 \mu_2 = 10^{-2} n_1 e_1 \mu_1$. Assume a magnitude for $|e|$ such that $n_1 e_1 = 1$, and let μ_1 have the "normal" value, -1 cm^2/V-sec. Then Eq. (8) becomes

$$\mu_H = \frac{-1 + 10^{-2}\mu_2}{1 + 10^{-2}} \approx 10^{-2}\mu_2 - 1. \tag{9}$$

Thus to account for the experimental values of μ_H, μ_2 must lie in the range 10^6 - 10^7 cm^2/V-sec and be positive. Admittedly, this is an extremely high value for μ_2, but it does illustrate the possibility that the behavior of two different transport coefficients can be vastly different from each other.

Another possible explanation that merits some attention is that some kind of resonant hopping of electrons between neighboring localized sites leads to an apparent high mobility. However, the only resonance we can think of which would lead to the relatively sharp peaks in the mobility-frequency curves is a spatial resonance due to the inevitable presence of well-defined atomic short-range-order (involving nearest- and perhaps next-nearest neighbors). But this type of resonance ought to depend on the electric field, since the distance travelled by a carrier in a given time interval is proportional to that field. No dependence on the electric field was observed.

Another difficulty with this approach is that the distance that a carrier travels during one cycle of the applied frequency is much larger than interatomic distances, even if a normal, low mobility is assumed. For example with $\mu = 1$ cm^2/V-sec, E = 1 volt/cm, and $t = 10^{-5}$ sec,

$$x = vt = \mu E t = 10^3 \text{ Å} . \tag{10}$$

It should be noted that the unusual mobility behavior was observed in amorphous semiconductors having room-temperature dc resistivities of about 10^7 ohm-cm. As mentioned earlier, we could not detect a Hall mobility signal in polystyrene, which has a much higher resistivity. We have studied the amorphous semiconductor, $Tl_2Se{\cdot}As_2Te_3$ which has a room-temperature resistivity of only 400 ohm-cm.[13] The Hall mobility in this material was of the order of 1 cm^2/v-sec, and was independent of frequency between 1 and 100 kHz.

Suppose that this last material also contained carriers of 1 and 10^6 cm^2/V-sec, that its lower resistivity was due to a 10^5 greater density of lower mobility carriers, and that its higher mobility carriers were present in about the same numbers as the present materials. Then Eq. (9) would become

$$\mu_H = \frac{10^5 + 10^{-2} \cdot 10^6}{10^5 + 10^{-2}} \approx 1 \tag{11}$$

Thus, the high-mobility carriers could be present in $Tl_2Se \cdot As_2Te_3$ also, but their presence would not be revealed by Hall mobility measurements.

Finally, we wish to note that the high mobility phenomenon in the two materials may be a consequence of the fact that they are threshold switching materials. The evidence is growing that this type of switching is not a purely thermal effect. It may be that the high mobility carriers which we have detected are involved in the electronic component of the threshold switching phenomenon.

Plans are underway to measure other materials, including some two component amorphous systems and at least one low carrier concentration crystalline semiconductor. Additional measurements on these and other materials will include a wider temperature range and possibly a wider frequency range. There is no way to predict whether frequency dependent high mobilities will be found in other amorphous, or even crystalline, semiconductors.

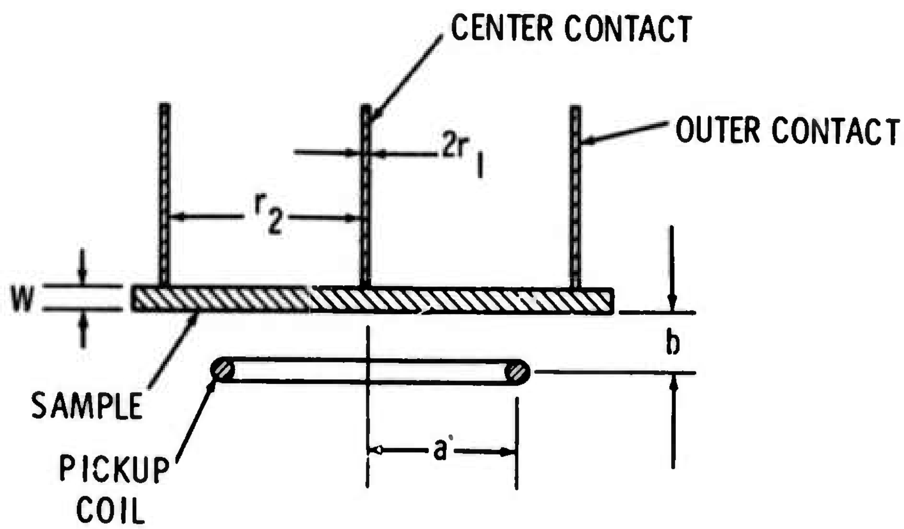


FIG. 1 CROSS SECTION OF THE CORBINO DISC WITH A ONE TURN PICKUP COIL

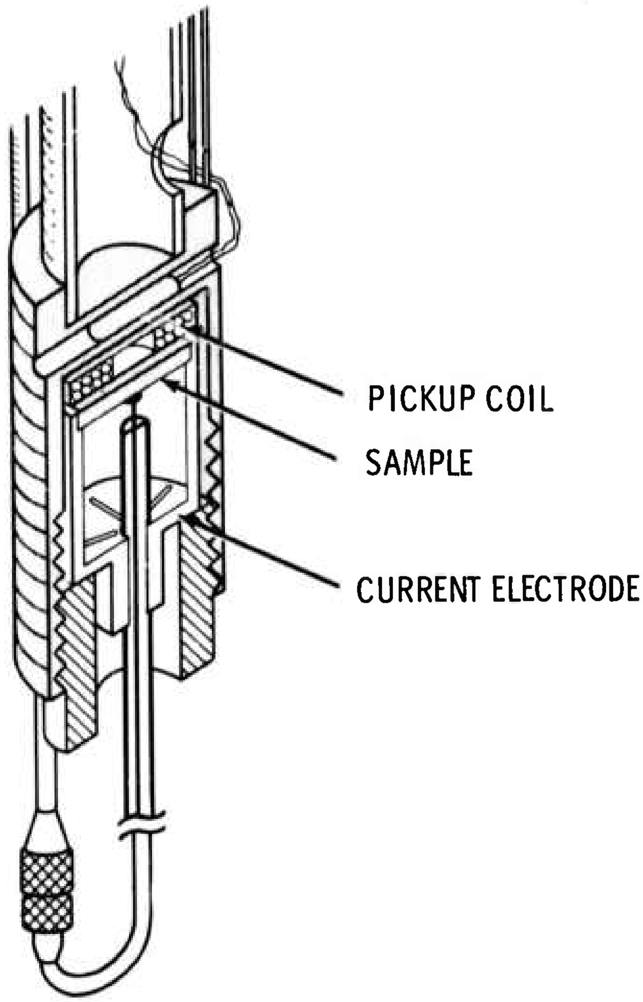


FIG. 2 CUT AWAY VIEW OF THE CORBINO SAMPLE HOLDER. THE COPPER CURRENT ELECTRODE HAS RADIAL SLOTS CUT INTO ITS TOP TO REDUCE CIRCULAR CURRENTS IN THE COPPER. THE CURRENT AND PICKUP COIL LEADS ARE STAINLESS STEEL JACKETED, RIGID COAXIAL CABLE.

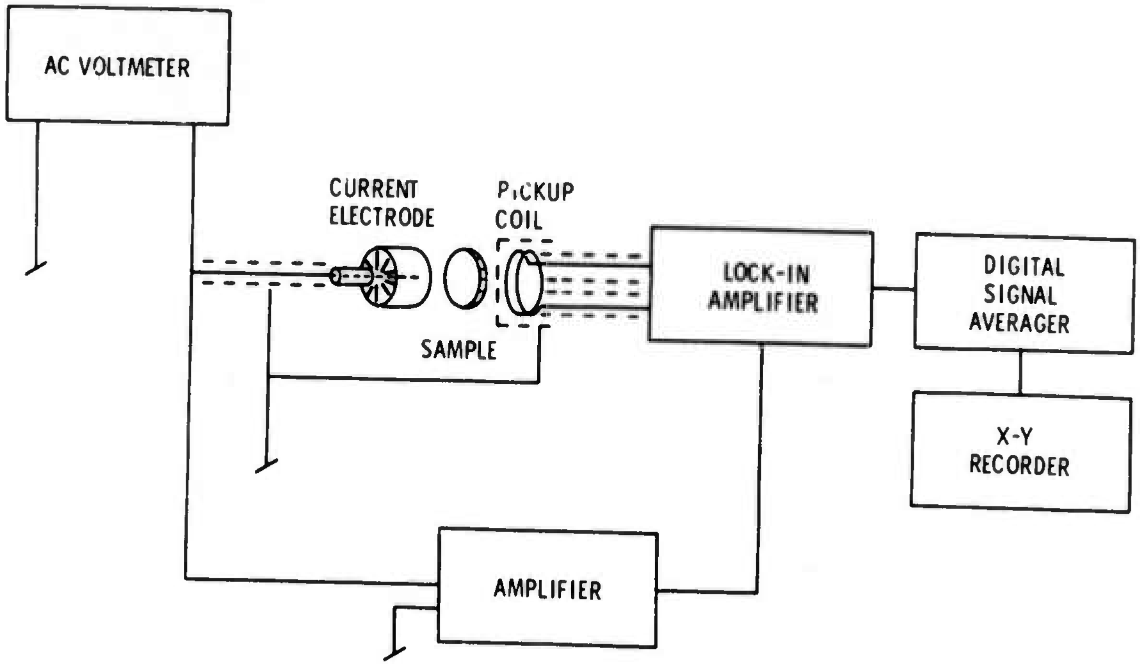


FIG. 3 BLOCK DIAGRAM OF THE CIRCUIT, INCLUDING A SCHEMATIC REPRESENTATION OF THE CORBINO DISC SAMPLE HOLDER.

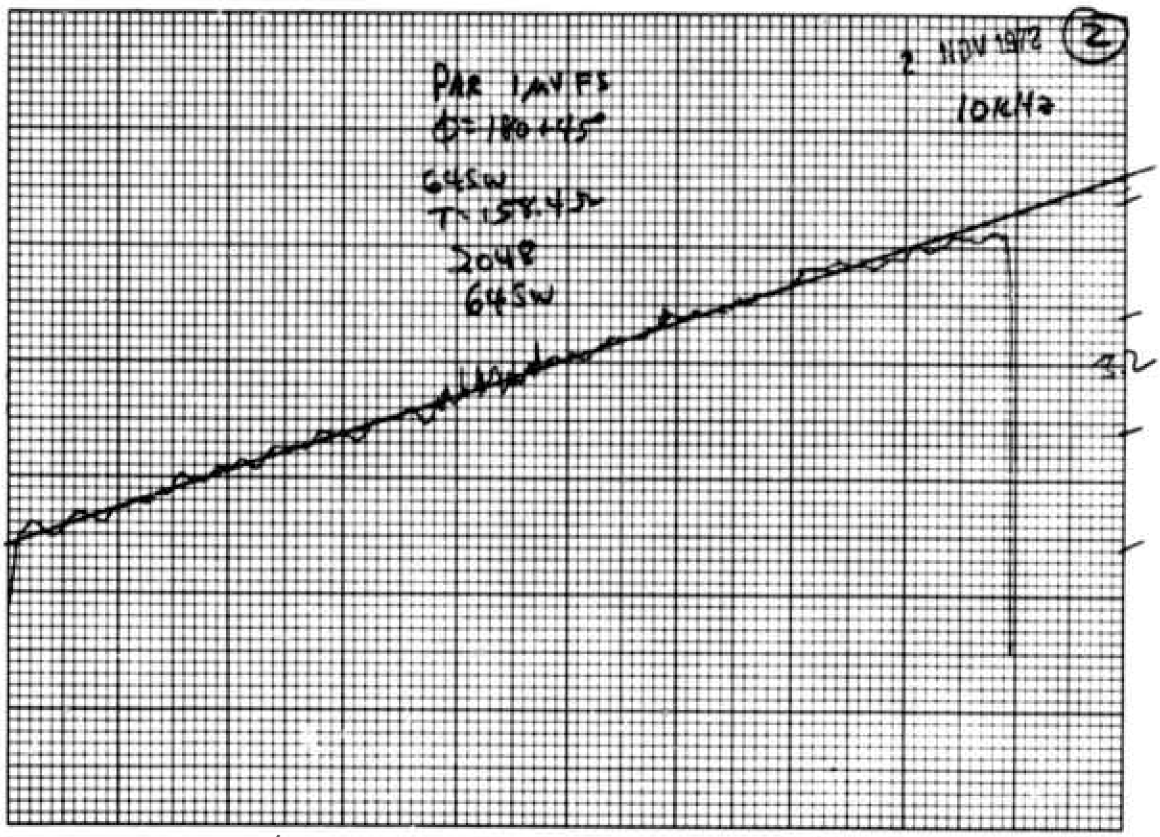


FIG. 4 EXAMPLES OF ACTUAL RECORDINGS OF THE MOBILITY DATA OF SAMPLE A-1 AT 220 K. THE SAMPLE VOLTAGE WAS 36 V. THE NUMBER OF SWEEPS (LABELED "SW"), THE RESISTANCE OF THE PLATINUM SENSOR (T), THE SENSITIVITY AND PHASE SETTING (ϕ) OF THE LOCK-IN DETECTOR, THE NUMBER OF COUNTS/INCH AS READ OUT FROM THE MEMORY OF THE SIGNAL AVERAGER, AND THE FREQUENCY ARE ALL MARKED ON THE TRACES. THE SIGNAL, TAKEN TO BE THE HEIGHT OF A LINE DRAWN THROUGH THE TRACE, IS MARKED AT THE RIGHT. (A BIT OF RECORDER NOISE IS EVIDENT ON SOME OF THE TRACES.) THE MAGNETIC FIELD IS SWEPT FROM ABOUT 0.1 TO 0.3 TESLA. THE TRACES ARE THE DIFFERENCE IN PICKUP VOLTAGE BETWEEN OPPOSITE DIRECTIONS OF THE MAGNETIC FIELD. (e) SHOWS THE MOST DRAMATIC KINK WHICH IS OBSERVED AT FREQUENCIES WHERE THE MOBILITY VS FREQUENCY IS CHANGING RAPIDLY. (f) AND (g) ARE MORE TYPICAL EXAMPLES OF THIS PHENOMENON.

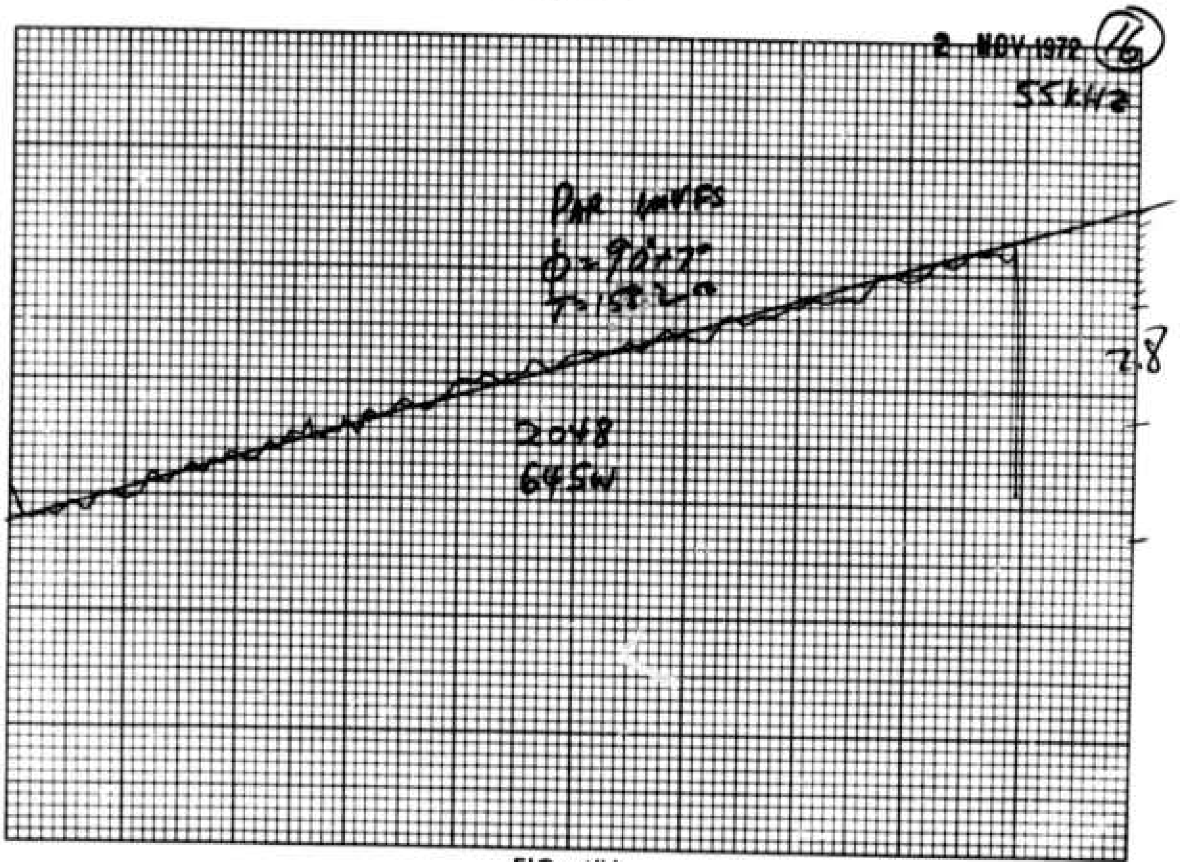


FIG. 4(b)

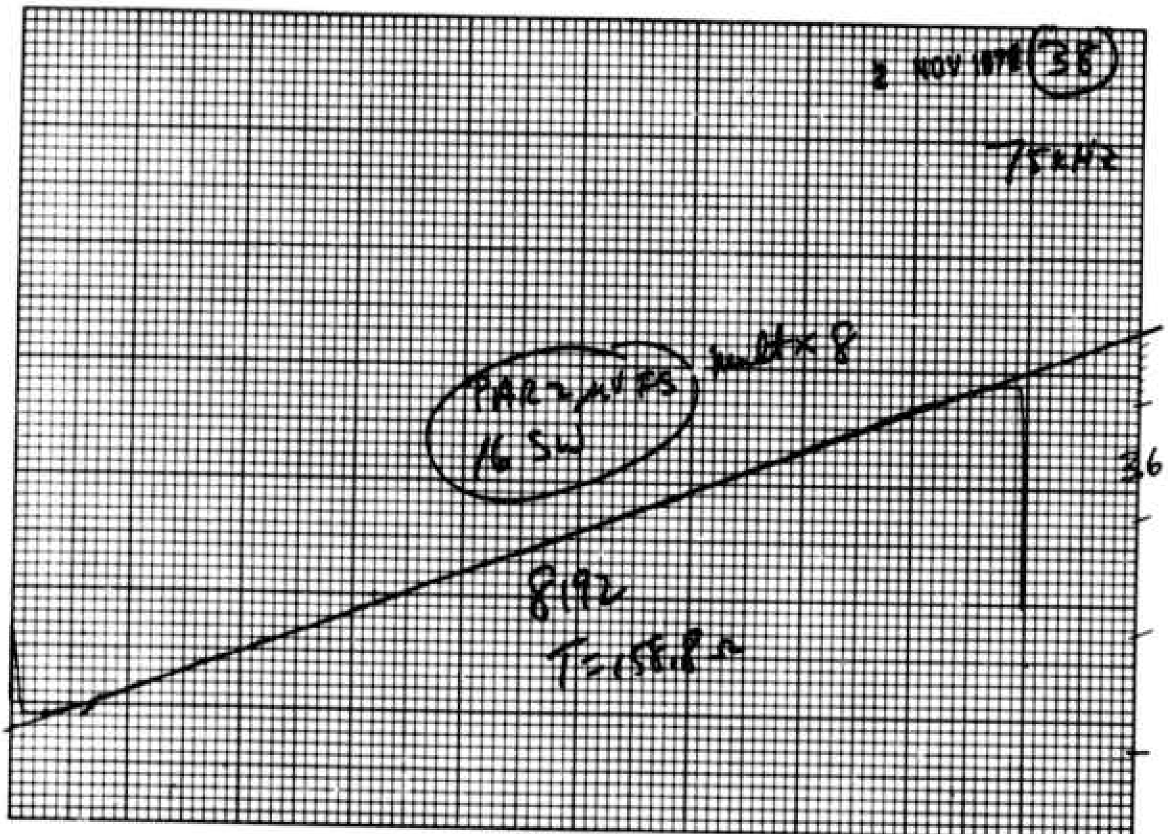


FIG. 4(c)

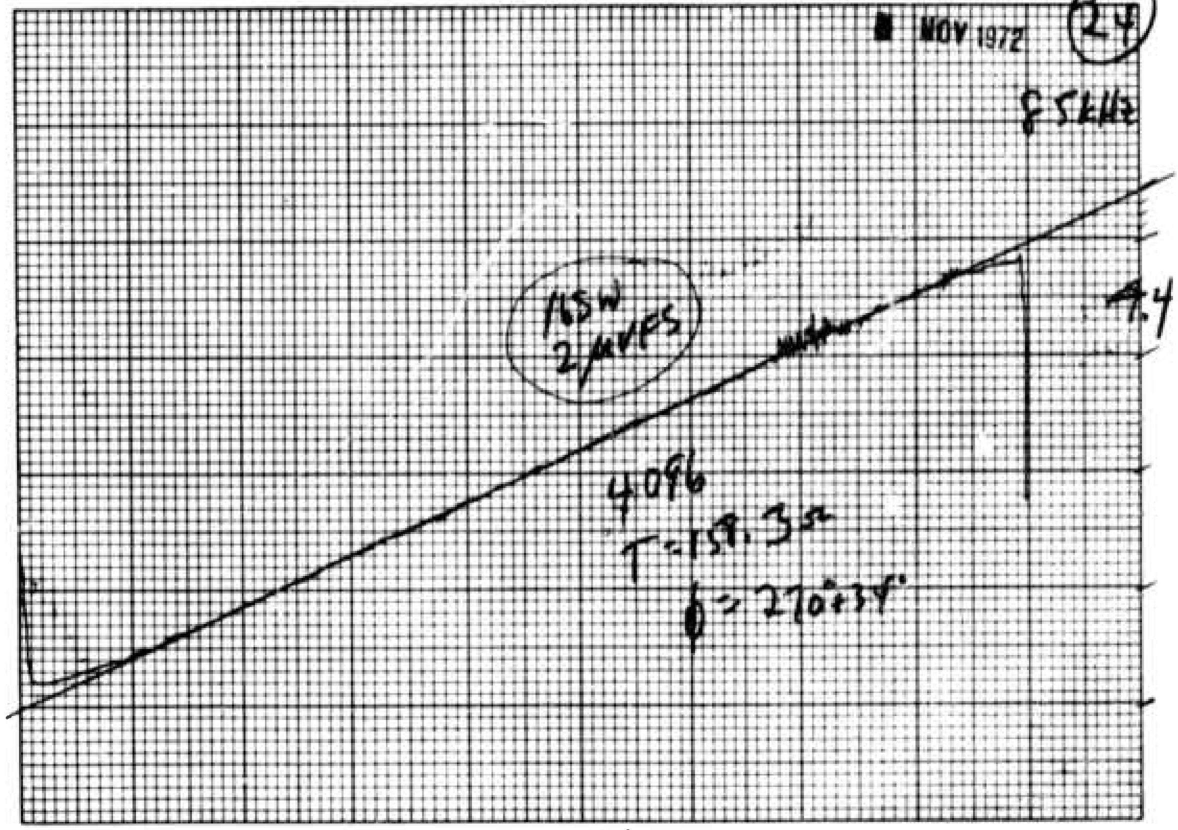

NOV 1972
24
8.5 kHz
4.4
15 SW
2 μVFS
4096
T = 158.3
φ = 270°+34°

FIG. 4(d)

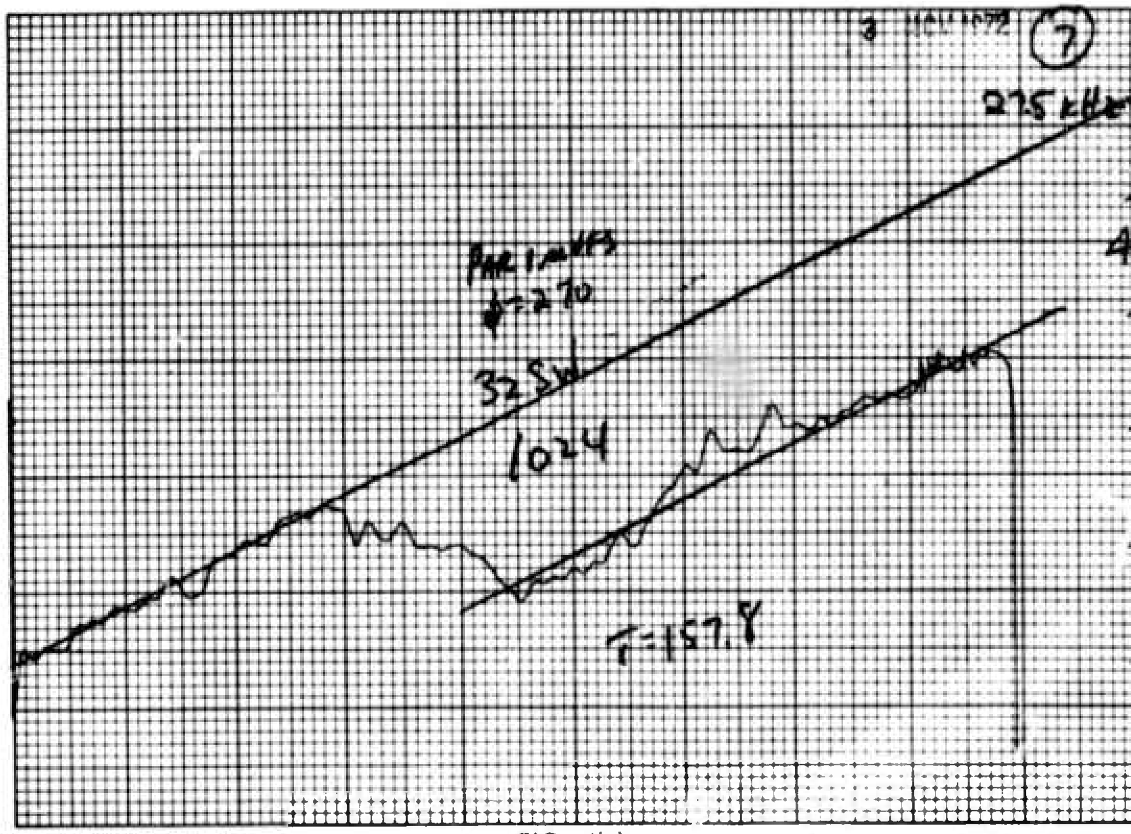

7
27.5 kHz
4.8
PAR 1 μVFS
φ = 270
32 SW
1024
T = 157.8

FIG. 4(e)

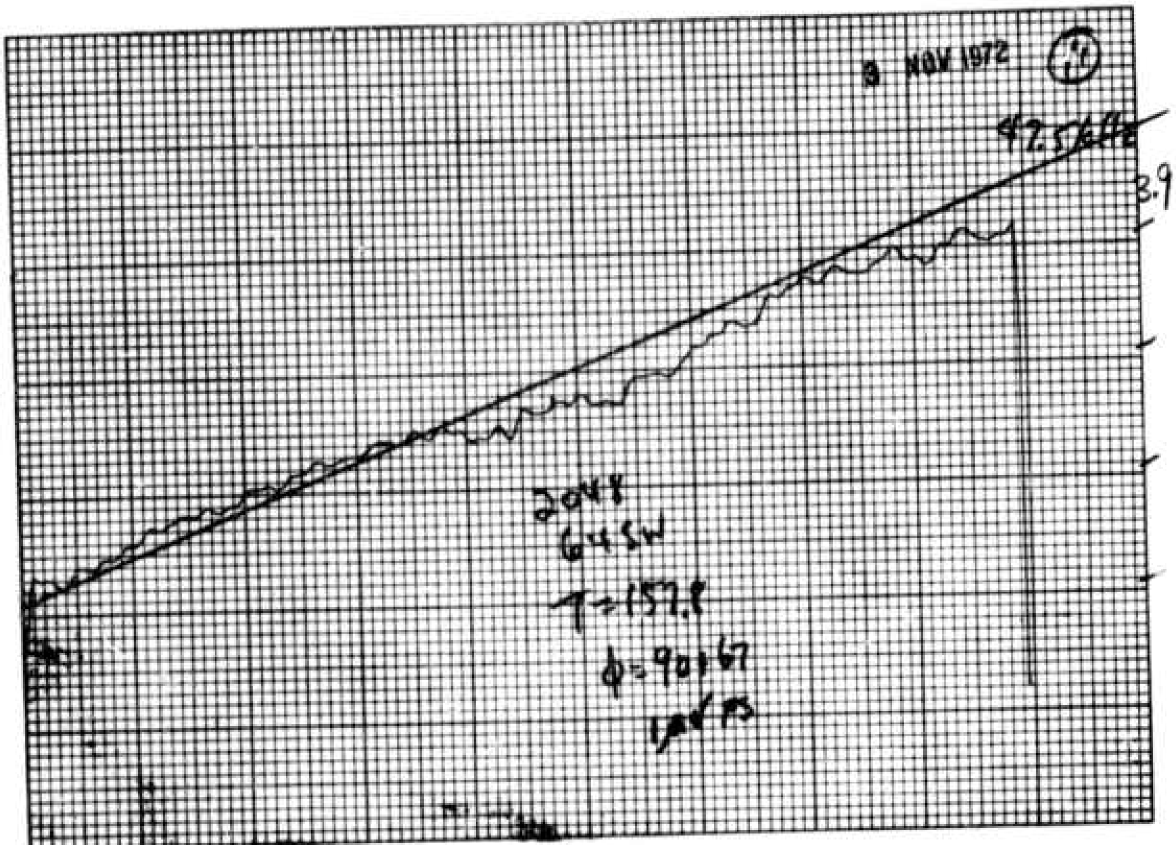

NOV 1972
42.5kHz
3.9
2048
64SW
T=157.8
φ=90+67
1μv FS

FIG. 4(f)

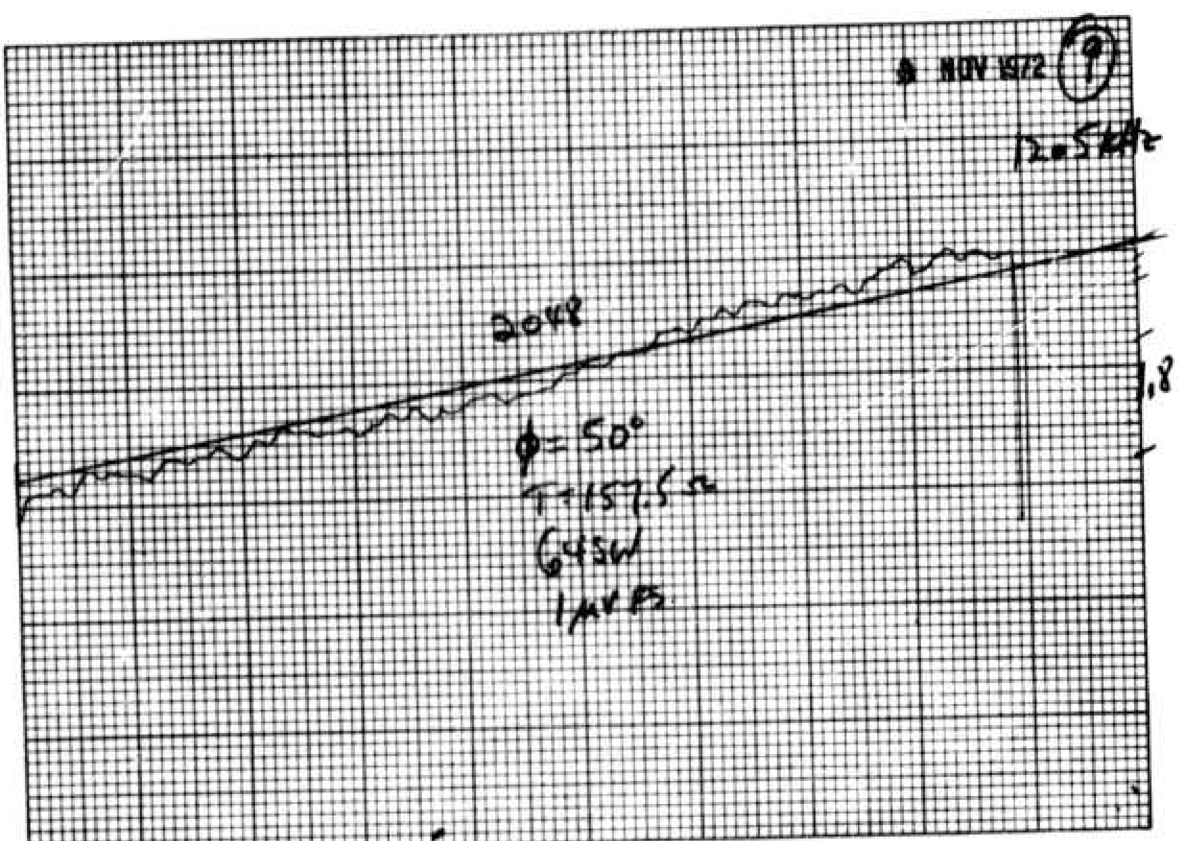

NOV 1972
12.5kHz
2048
1.8
φ=50°
T=157.5
64SW
1μv FS

FIG. 4(g)

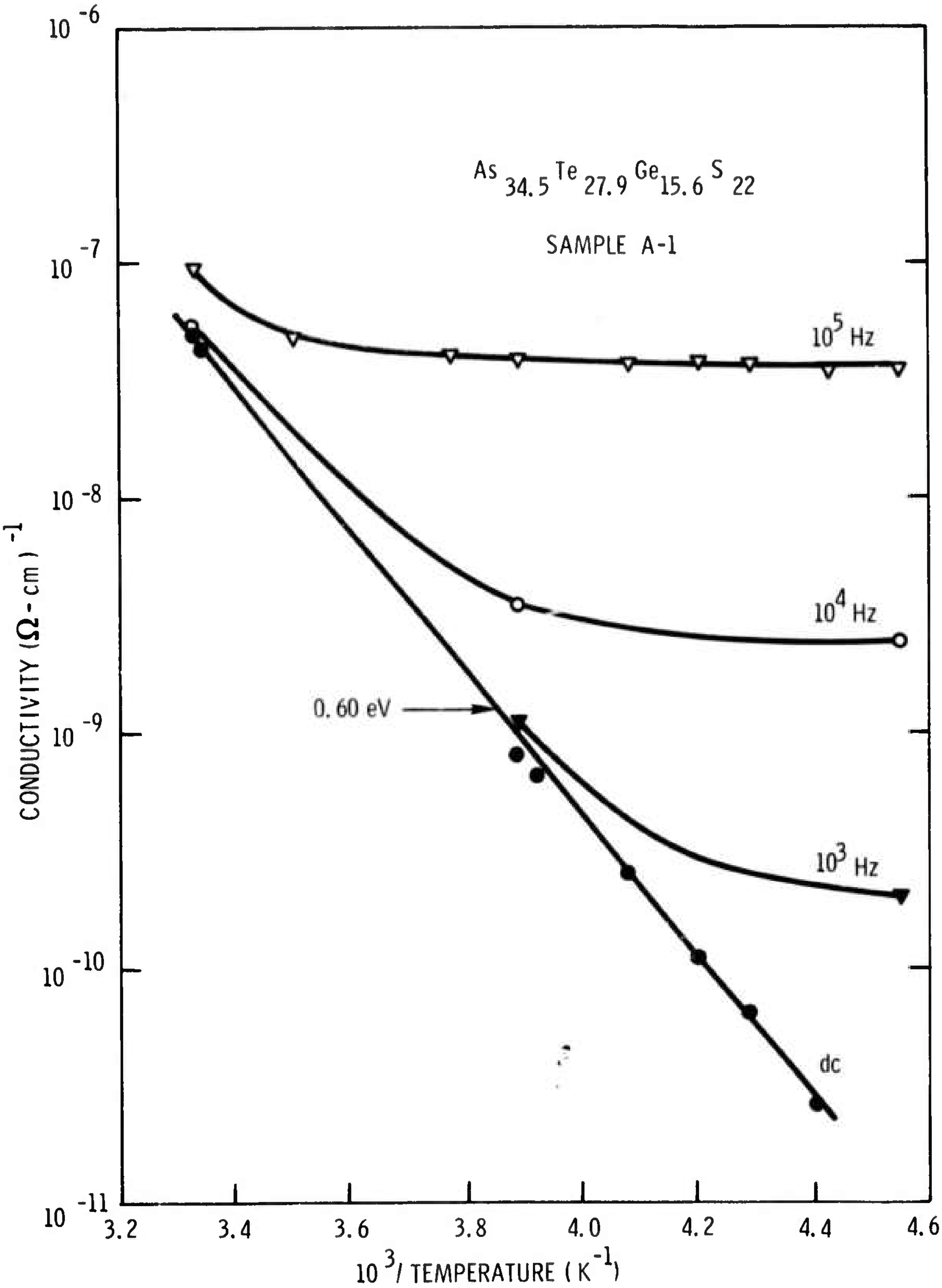


FIG. 5 THE CONDUCTIVITY AS A FUNCTION OF TEMPERATURE FOR SAMPLE A-1

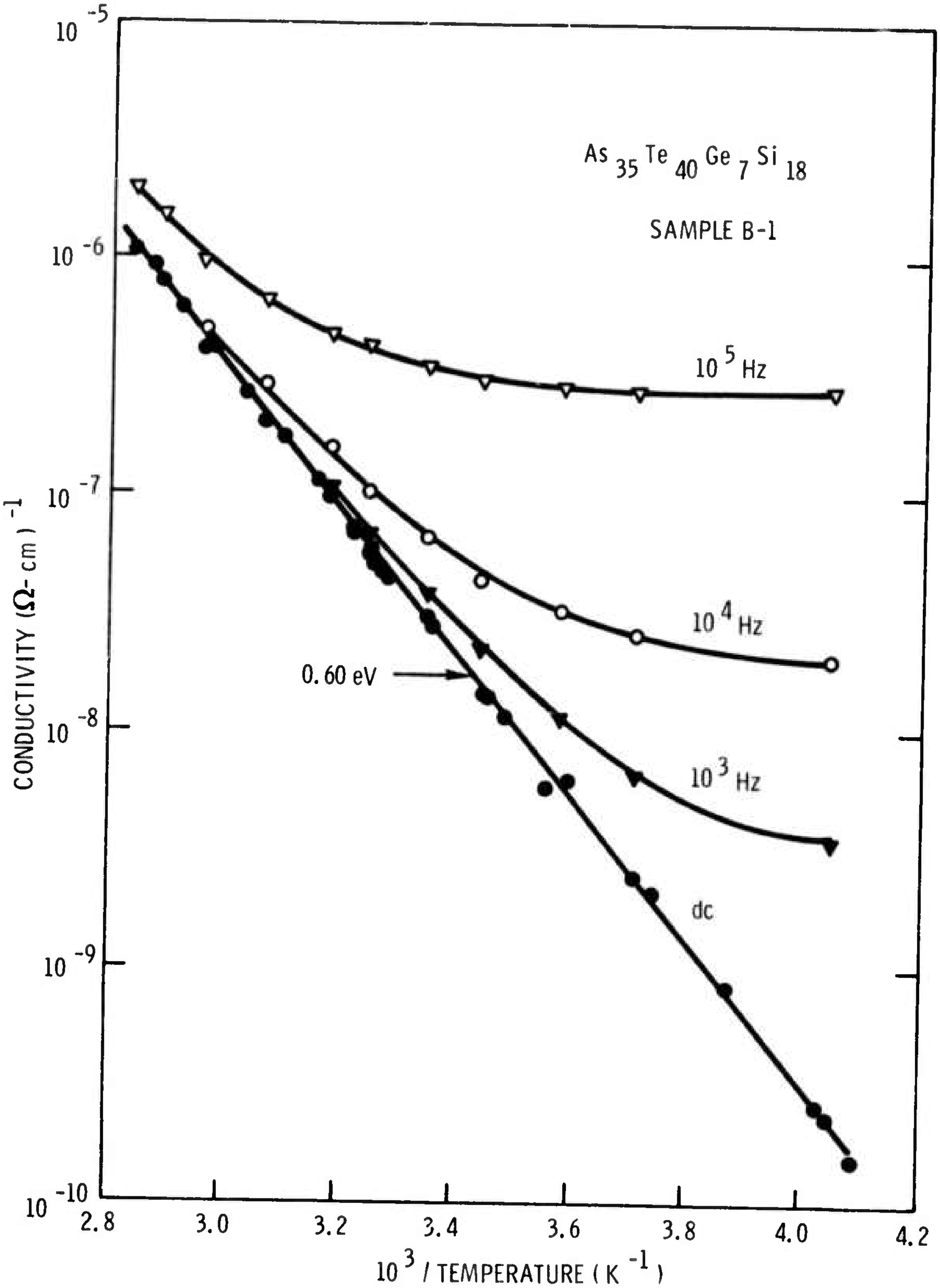


FIG. 6 THE CONDUCTIVITY AS A FUNCTION OF TEMPERATURE FOR SAMPLE B-1

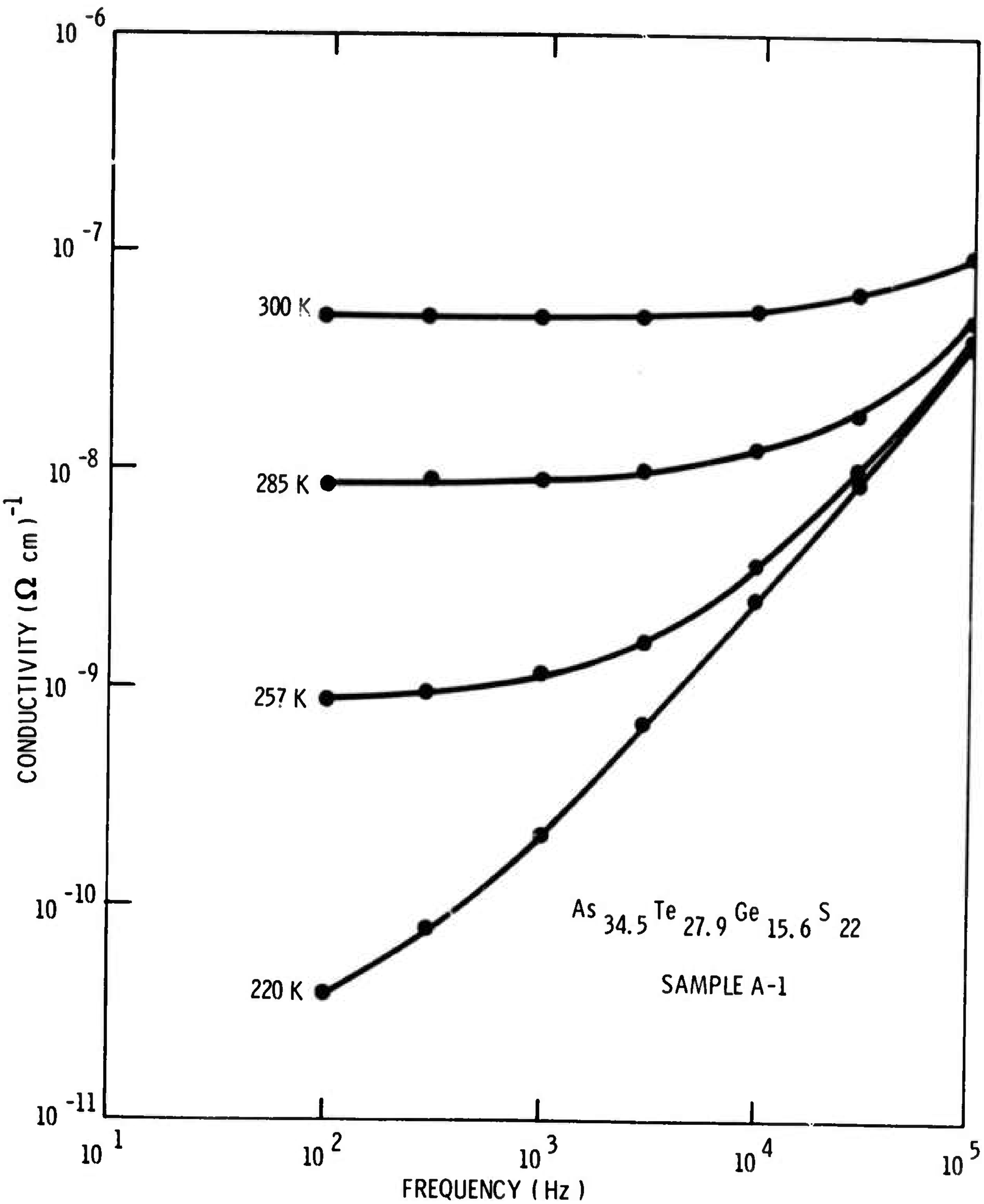


FIG. 7 THE FREQUENCY DEPENDENCE OF THE CONDUCTIVITY FOR SAMPLE A-1

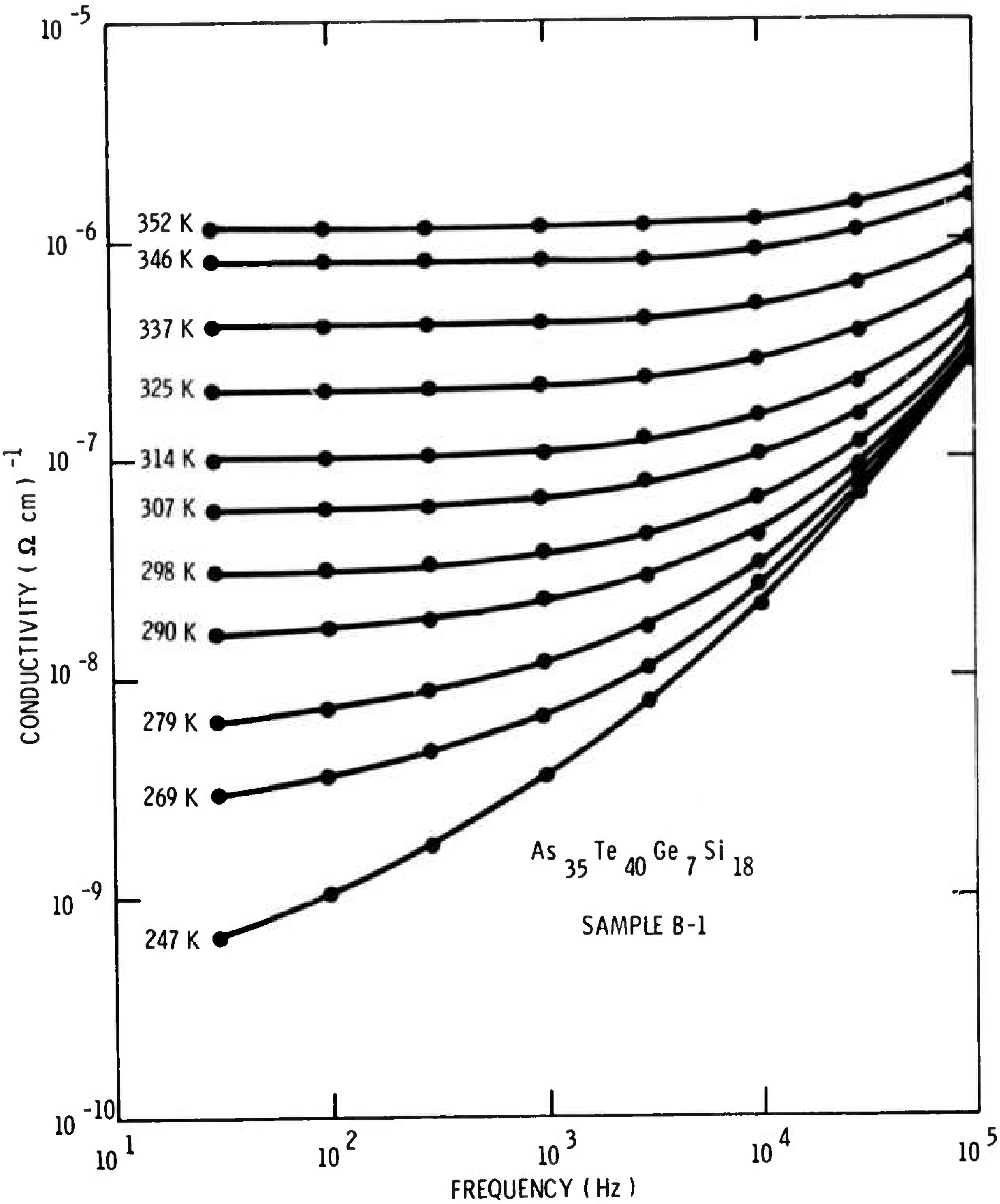


FIG. 8 THE FREQUENCY DEPENDENCE OF THE CONDUCTIVITY FOR SAMPLE B-1

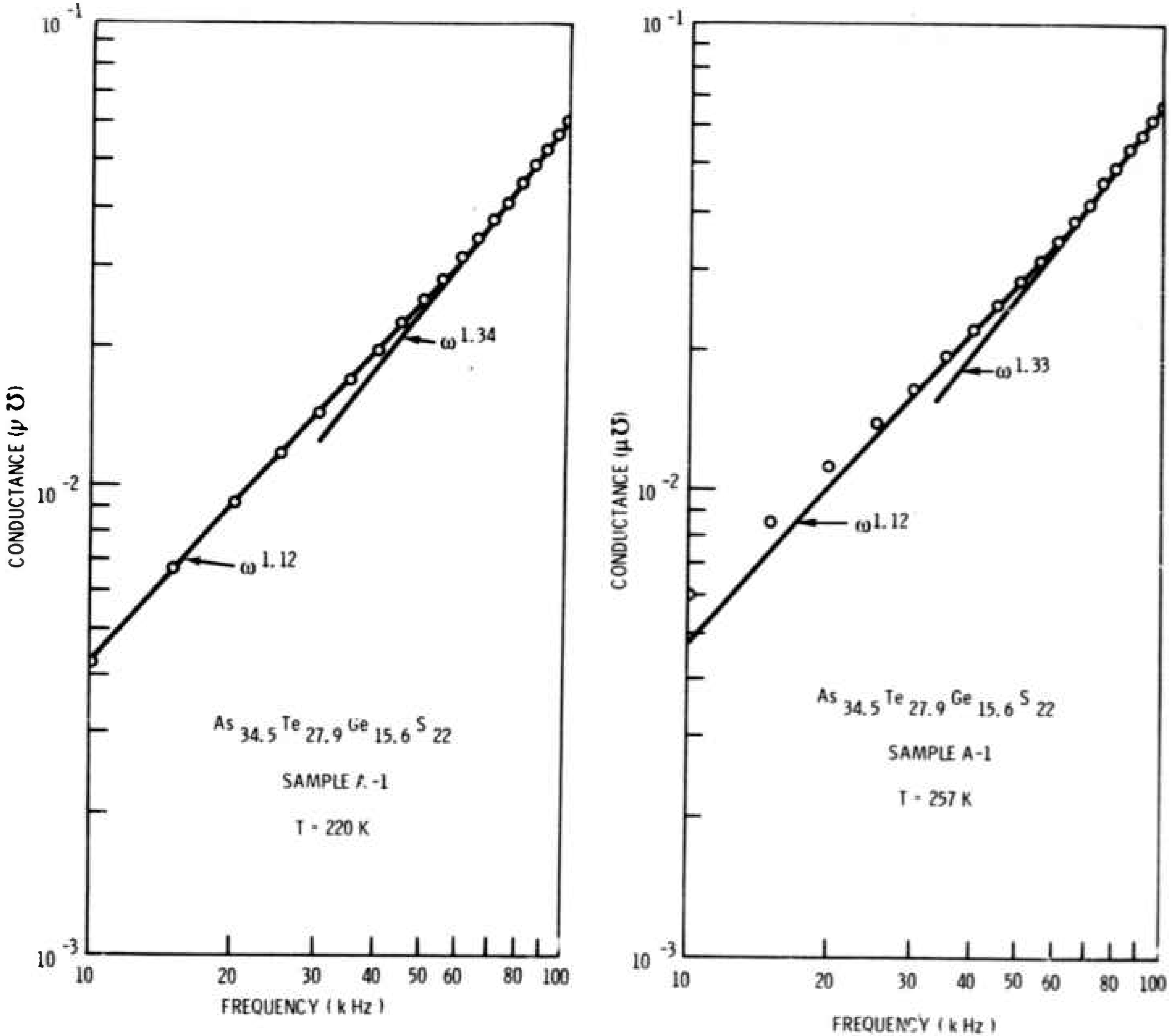


FIG. 9 THE CONDUCTANCE OF SAMPLE A-1 BETWEEN 10 AND 100 kHz FOR THE TWO TEMPERATURES AT WHICH MOBILITY MEASUREMENTS WERE MADE

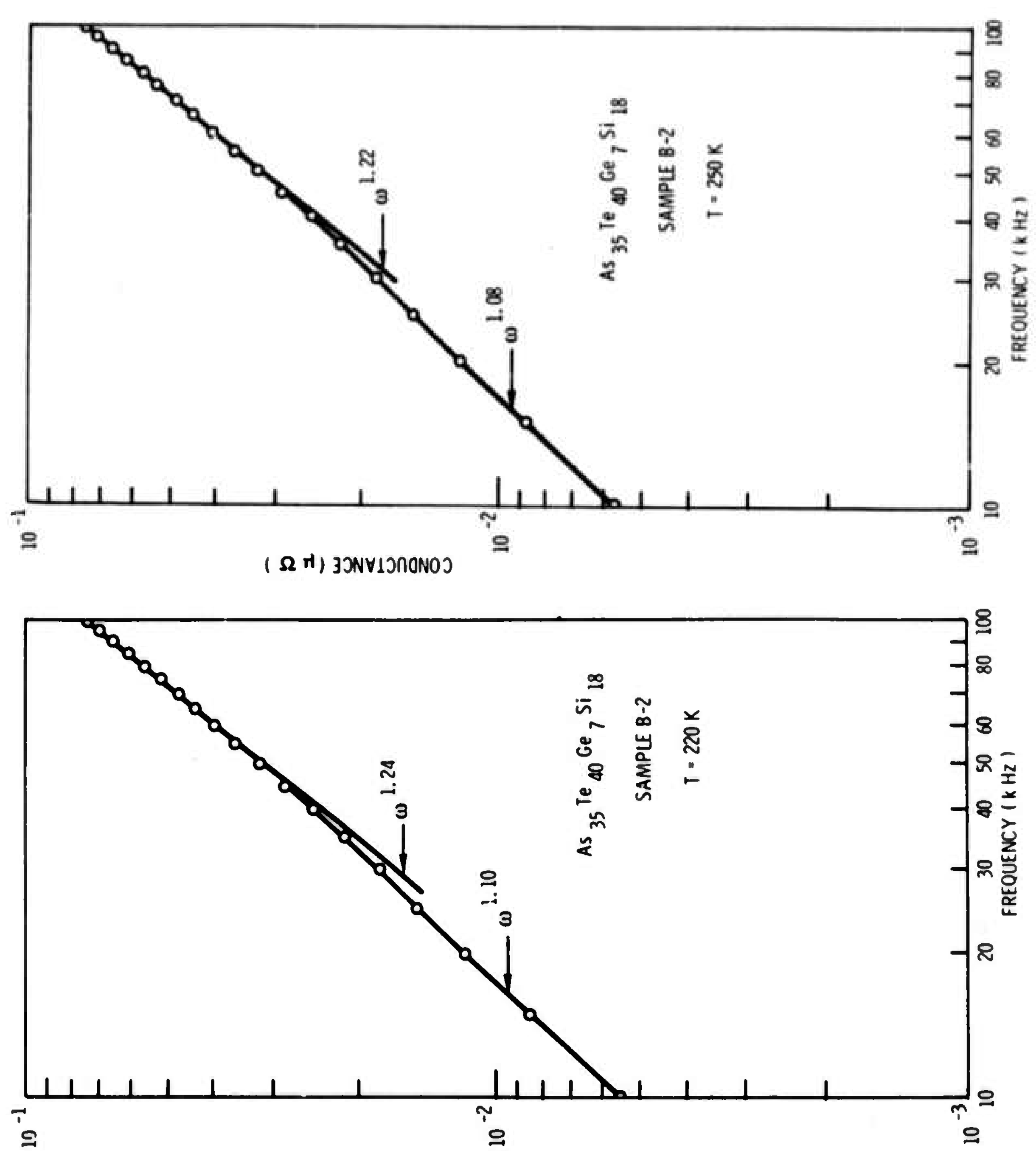


FIG. 10 THE CONDUCTANCE OF SAMPLE B-2 BETWEEN 10 AND 100 kHz

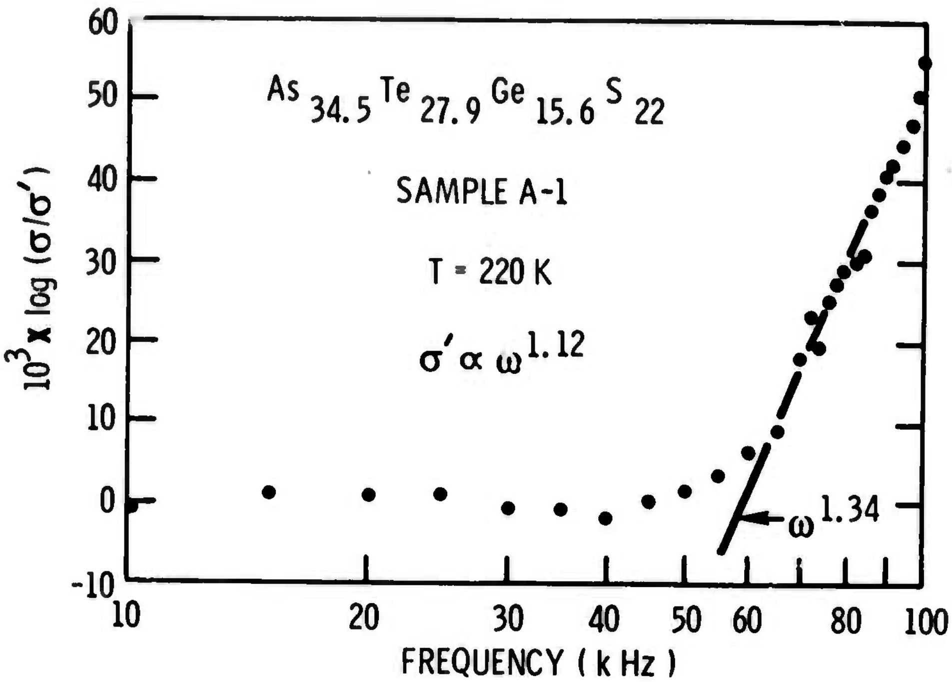
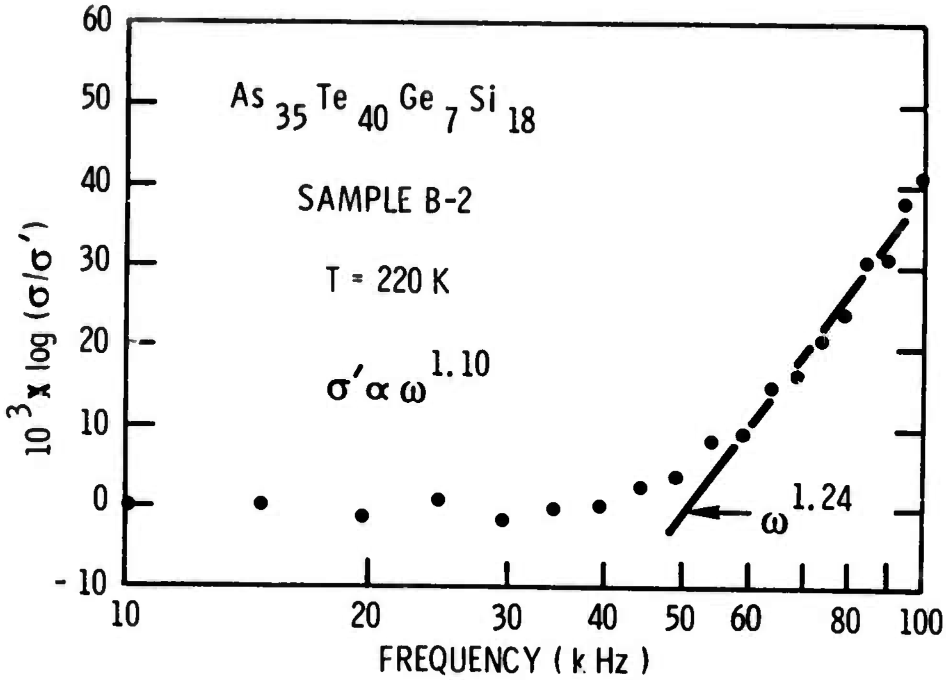


FIG. 11 COMPUTER FIT TO THE CONDUCTANCE G, OF SAMPLE A-1 AT 220 K ILLUSTRATING THE CHANGE IN THE SLOPE OF G VS FREQUENCY WHICH OCCURS AT ABOUT 60 kHz



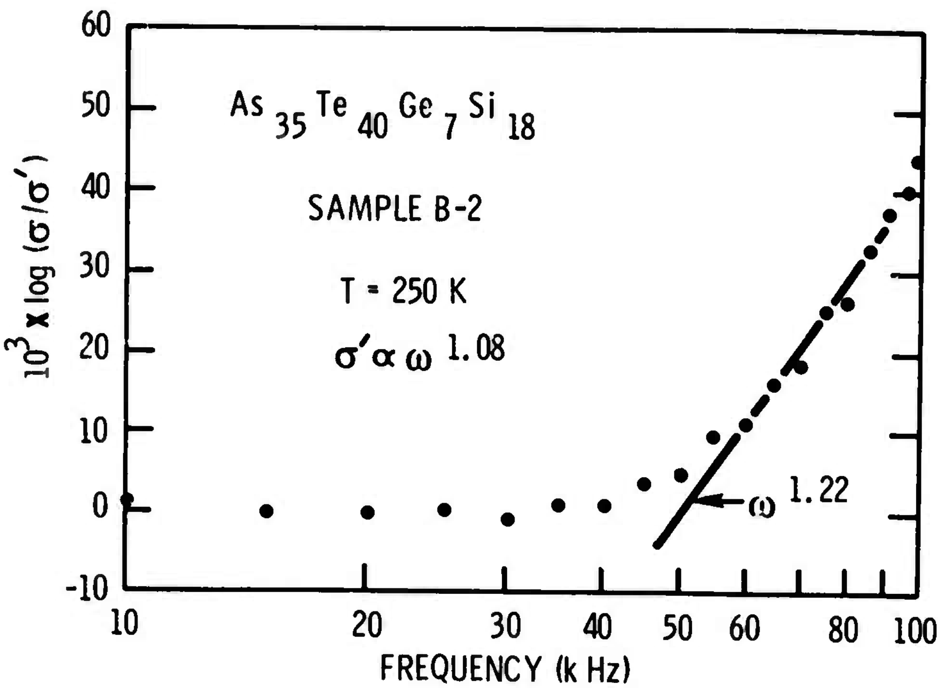


FIG. 12 COMPUTER FIT TO THE CONDUCTANCE DATA OF SAMPLE B-2

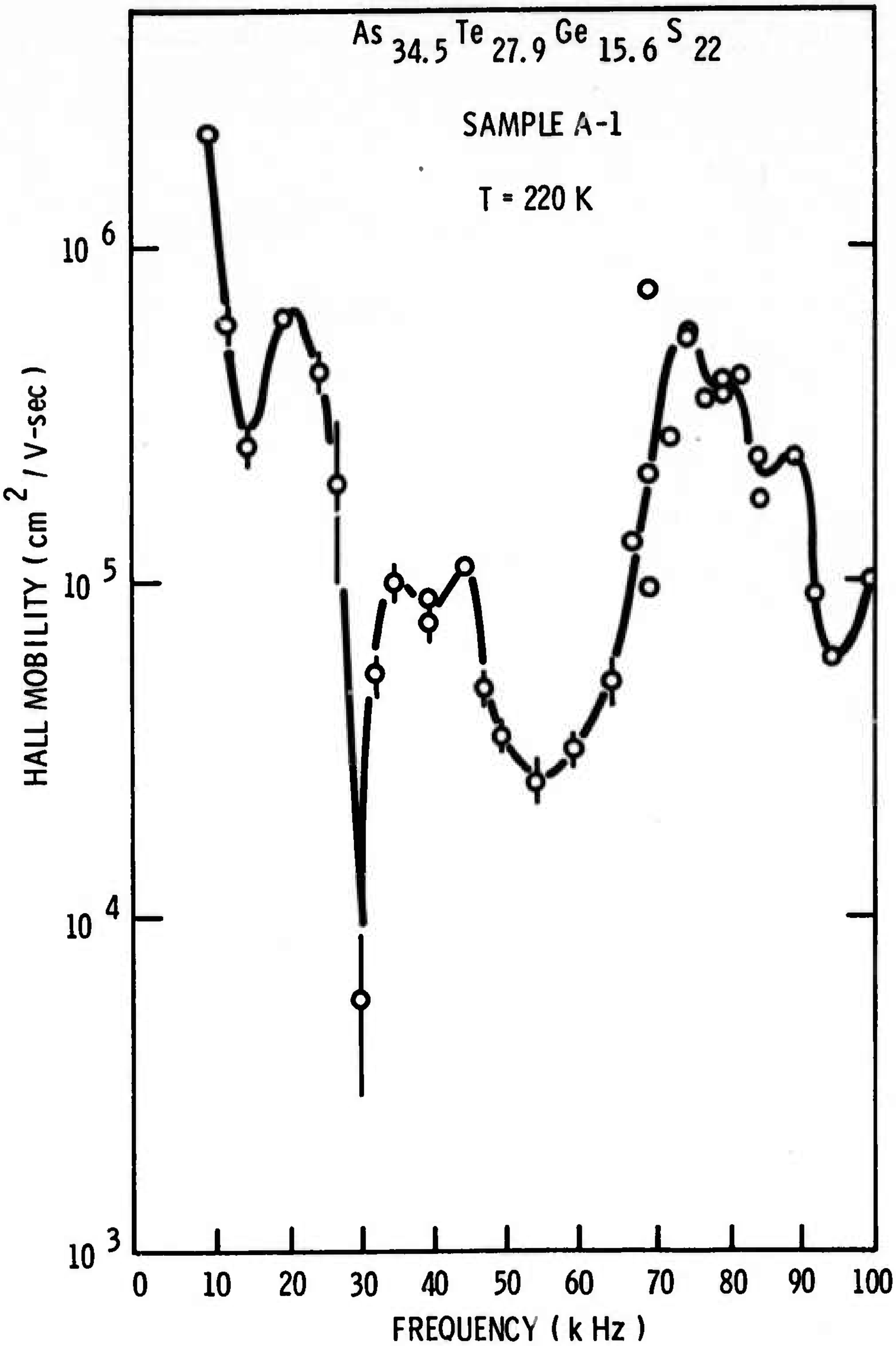


FIG. 13 THE HALL MOBILITY AS A FUNCTION OF FREQUENCY FOR SAMPLE A-1 AT 220 K. THE ERROR LIMITS REPRESENT ESTIMATES OF THE UNCERTAINTY BASED UPON UNCERTAINTIES IN THE SIGNAL MEASURED ON THE TRACES AND UNCERTAINTIES IN OTHER RELEVANT PARAMETERS OF THE MEASUREMENT. SYSTEMATIC ERRORS WHICH MAY BE PRESENT, SUCH AS CALIBRATION ERRORS AND UNKNOWN EFFECTS WHICH SOMETIMES MAY CAUSE THE REPRODUCIBILITY TO FALL OUTSIDE THE ESTIMATED RANDOM ERROR LIMITS, ARE NOT INCLUDED.

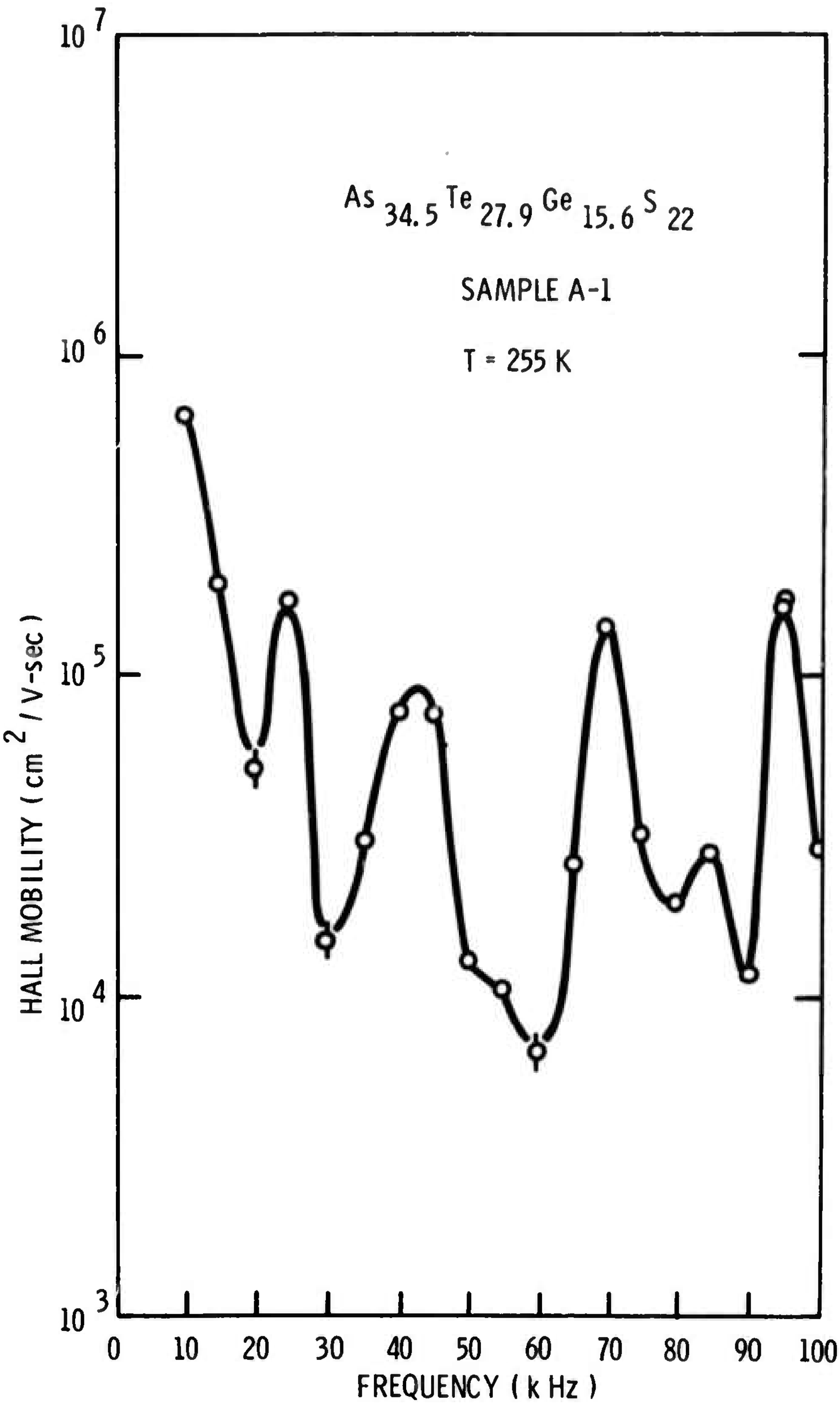


FIG. 14 THE HALL MOBILITY AS A FUNCTION OF FREQUENCY FOR SAMPLE A-1 AT 255 K

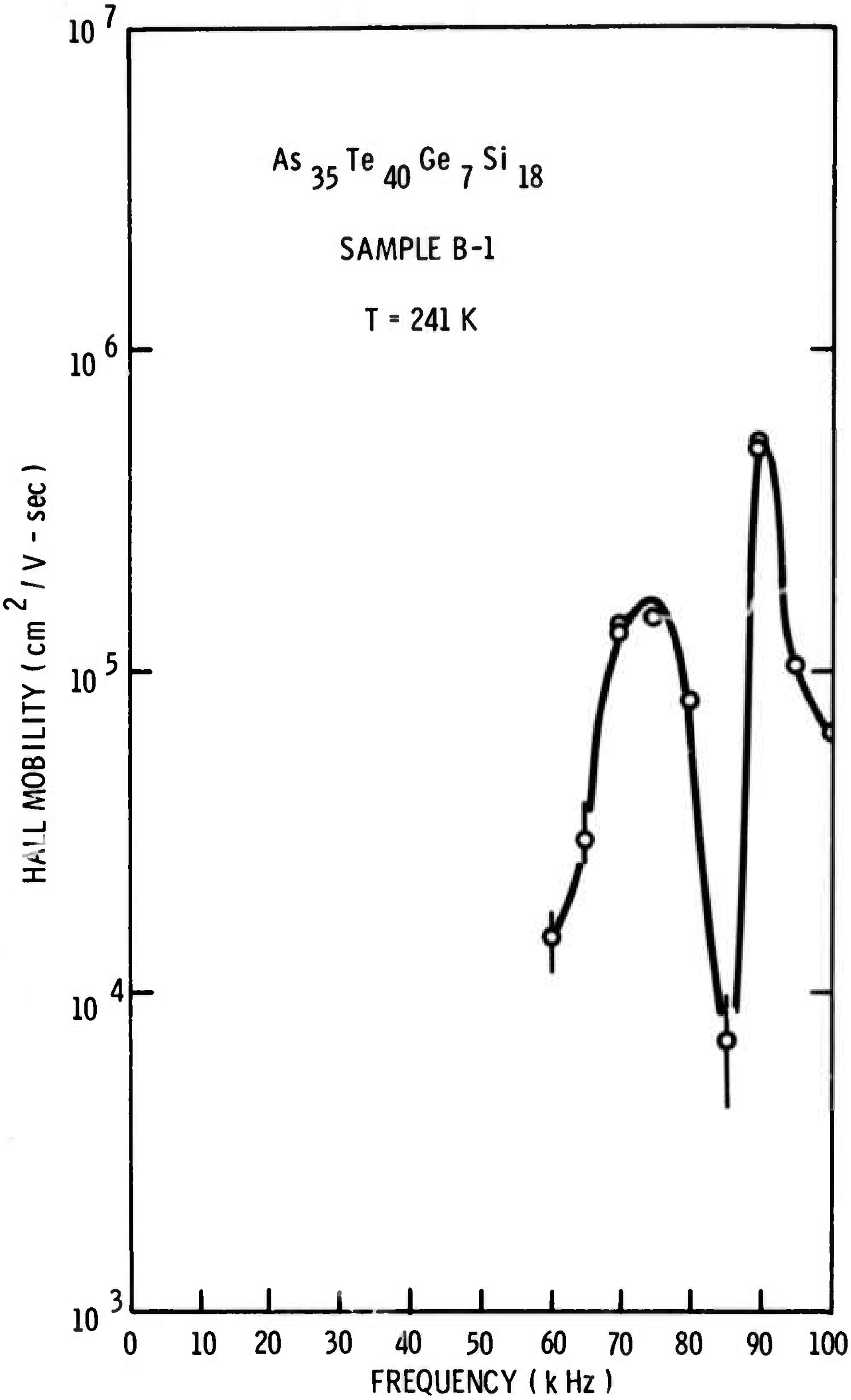


FIG. 15 THE HALL MOBILITY AS A FUNCTION OF FREQUENCY FOR SAMPLE B-1 AT 241 K

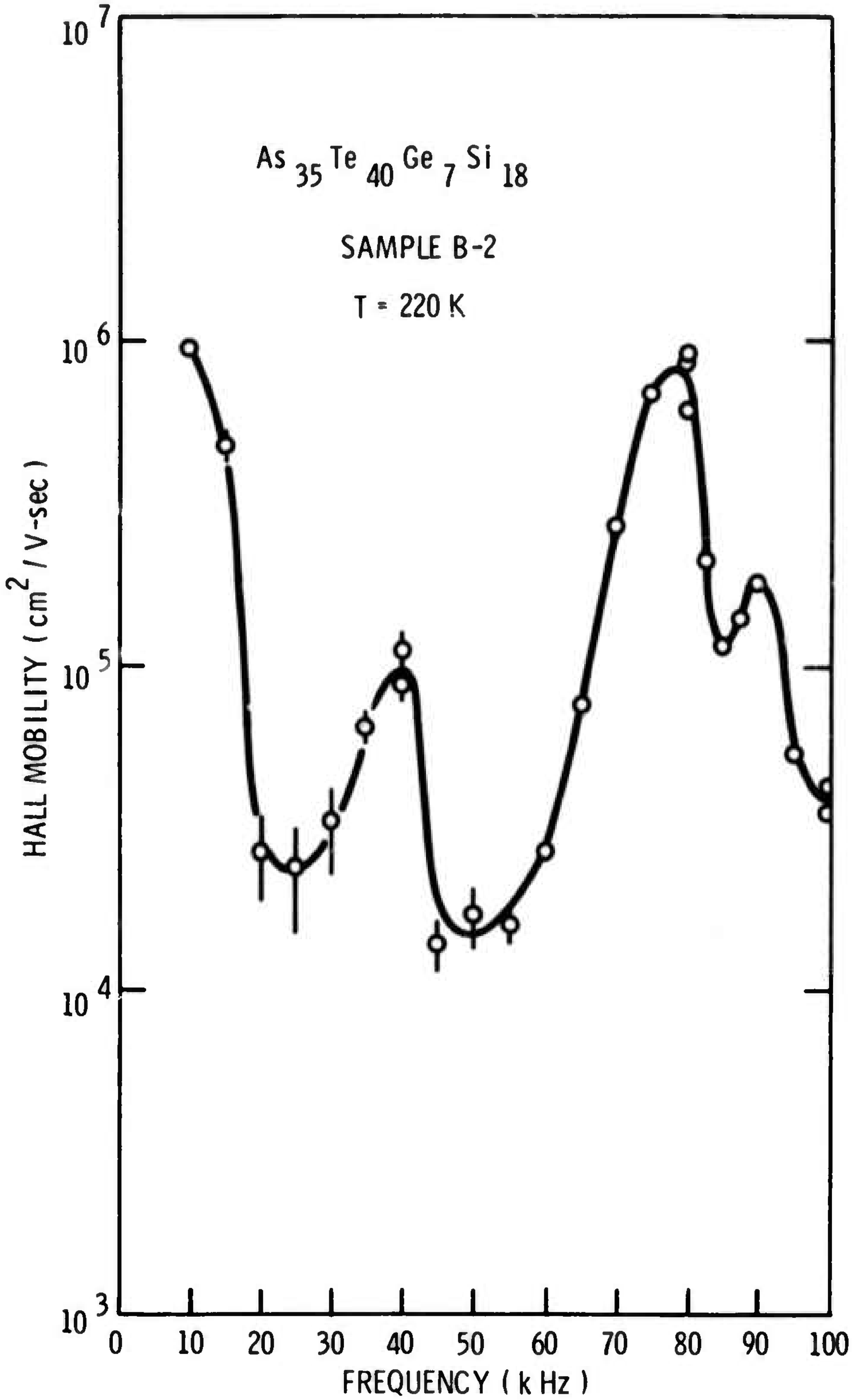


FIG. 16 THE HALL MOBILITY AS A FUNCTION OF FREQUENCY FOR SAMPLE B-2 AT 220 K

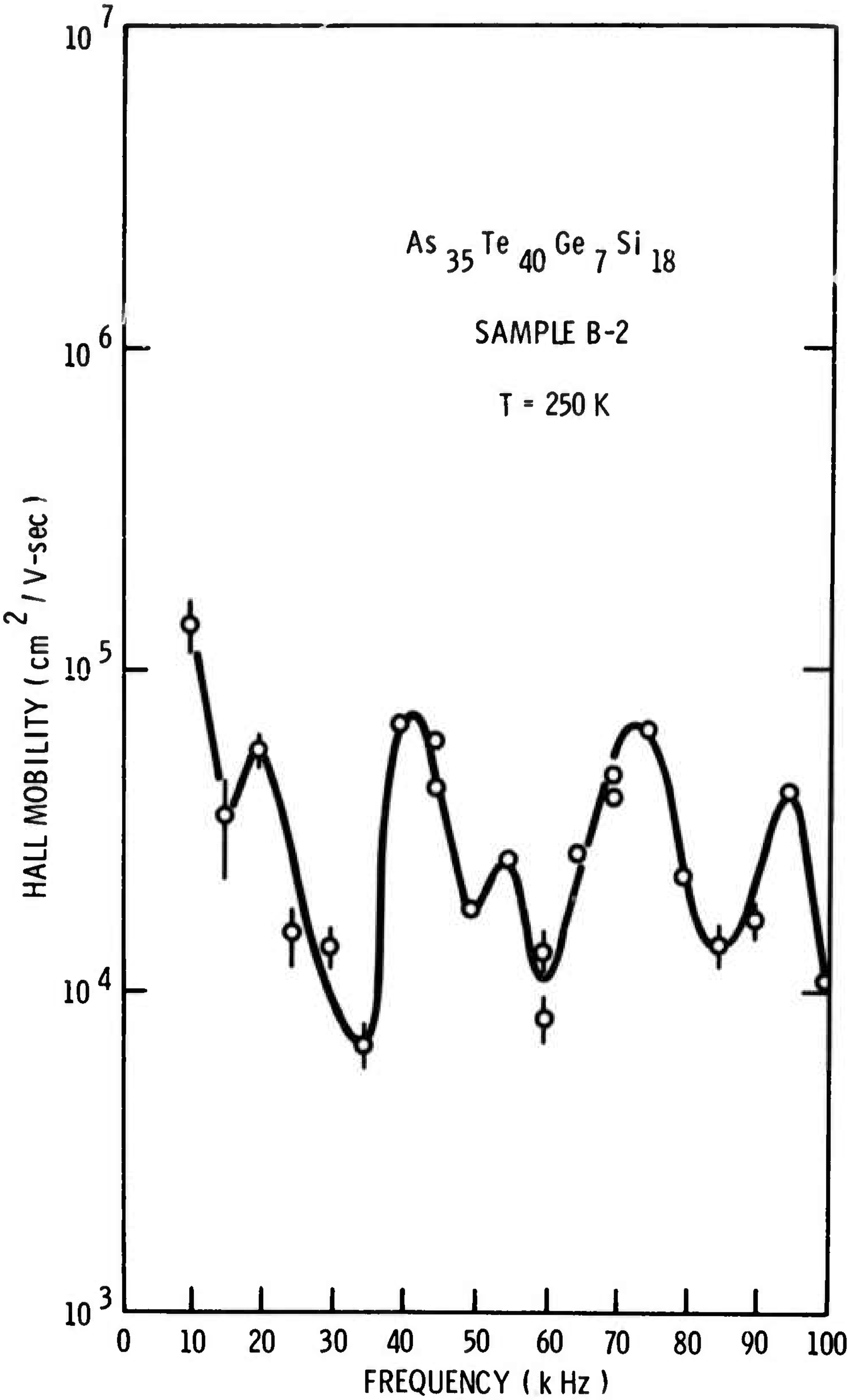


FIG. 17 THE HALL MOBILITY AS A FUNCTION OF FREQUENCY FOR SAMPLE B-2 AT 250 K

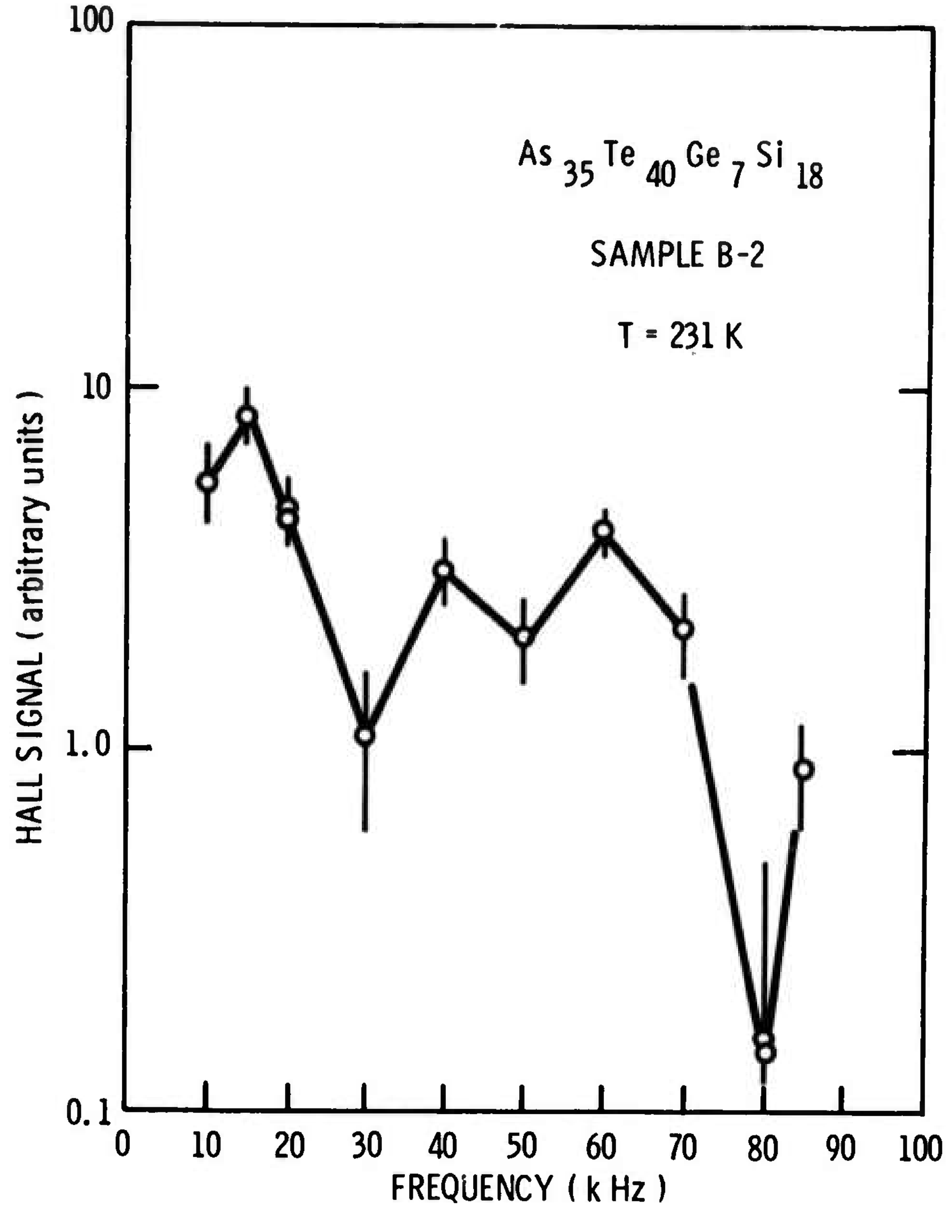


FIG. 18 THE HALL SIGNAL, OBTAINED USING A FOUR-POINT VAN DER PAUW CONFIGURATION, FOR SAMPLE B-2 AT 231 K

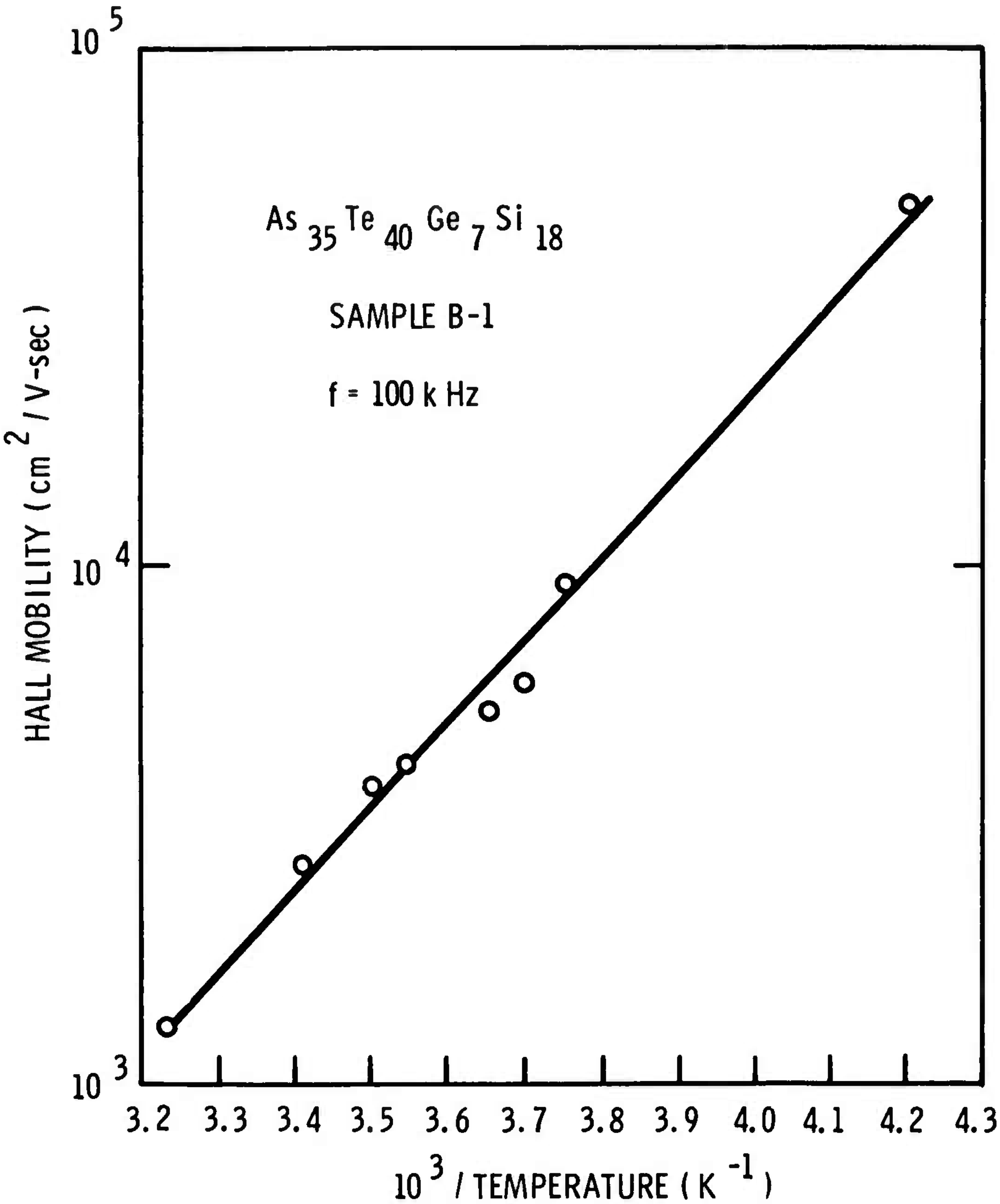


FIG. 19 THE HALL MOBILITY AT 100 kHz AS A FUNCTION OF TEMPERATURE FOR SAMPLE B-1